

# MODELING OF 2-BROMOTRIFLUOROPROPENE FLAME INHIBITION

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## Introduction

We have developed a new chemical mechanism for modeling flame inhibition by 2-bromotrifluoropropene (2-BTP). The modeling results qualitatively predicted agent behavior in cup-burner and FAA Aerosol Can tests over a wide range of conditions. The ban on high ozone depletion potential (ODP) chemicals requires replacement agents to be identified. To-date, there are no alternative agents meeting both FAA minimum performance and minimum ODP standards for protecting passenger aircraft cargo-bays.

In this work, we used high level *ab initio* calculations to compute energies of molecules and transition states and RRKM/Master Equation modeling to compute rate expressions to supplement available thermochemical and chemical kinetic data. This information was used to construct a mechanism for modeling flame inhibition, employing the new 2-BTP mechanism with the established USC Mech 2.0 hydrocarbon mechanism, an updated version of the NIST HFC sub-mechanism for hydrofluorocarbons, and an updated CF<sub>3</sub>Br sub-mechanism.

We provide here a short overview of our mechanism development and modeling of the flame inhibition by 2-BTP.

## Mechanism

The full mechanism consists of several of sub-mechanisms.

**Hydrocarbon Decomposition and Oxidation Chemistry.** The base hydrocarbon decomposition and oxidation chemistry was taken from the well-validated USC Mech 2.0 (2007).<sup>1</sup> This sub-mechanism has about 100 species and 800 reactions. We provided an update to this mechanism to include additional reactions involving hydrocarbon oxidations steps. These reactions were taken from the Princeton ethanol decomposition model (2004).<sup>2</sup>

**Hydrofluorocarbon Chemistry.** This chemistry is based on the NIST HFC C1-C2 mechanism (1995)<sup>3</sup> that describes the decomposition and oxidation chemistry of hydrofluorocarbons. To this, we have added updates and refinements of this sub-mechanism based on work at NIST, NRL, and Princeton (1998-2012).<sup>4,5,6</sup> In addition, in this work, we added a number of additional reactions involving F and F<sub>2</sub> which are present for high loadings of fluorine-containing agents.

**Bromine and Brominated-Hydrocarbon Chemistry.** The base bromine and brominated hydrocarbon chemistry was taken from the NIST CF<sub>3</sub>Br mechanism (1996).<sup>7</sup> That mechanism was an update of the mechanism originally developed by Westbrook (1980).<sup>8</sup> The current sub-mechanism includes more recent updates by Dixon-Lewis et al (2012)<sup>9</sup> and others.

**2-Bromotrifluoropropene Chemistry.** In this work, we developed a new mechanism for the decomposition and oxidation chemistry of 2-bromotrifluoropropene (2-BTP). We used high level

*ab initio* model chemistry (G3MP2B3)<sup>10</sup> calculations to compute energies of molecules to supplement available thermochemical data in the literature. We also used these methods to compute the energies of transition states coupled with transition state theory or RRKM/Master Equation modeling to compute rate expressions for critical reactions where there were no direct experimental data or good analogies where available. Although we have used this new sub-mechanism to model the flame inhibition by 2-BTP and it performs adequately, this new sub-mechanism should be considered as a first version that will need to be revised through its use for modeling a wider range of conditions and with detailed comparison with specific experimental determinations such as flame speeds, temperature profiles, or product sampling.

## Mechanism Development.

In this work, we first drafted a preliminary mechanism with most possible pathways and having many species and reactions – ignoring energetics as a consideration. We compiled and evaluated thermochemical and chemical kinetic data in the literature for the relevant species and reactions. We then computed (or estimated) the enthalpy of each reaction, and eliminated those reactions that were not energetically feasible by comparison to other reactions.

The mechanism was then revised, and we employed *ab initio* calculations to compute the energies of molecular species and transition states where no experimental data were available, or where no good analogy existed. In these calculations, we employed reference species and reactions (where experimental data exist) to benchmark our quantum chemical calculations.

This initial revised model was employed in modeling the decomposition, oxidation, and inhibition chemistry of 2-BTP. Again, we revised the mechanism to reflect the important species and significant reactions that were identified in the modeling results, and employed this revised mechanism as the basis for our modeling of flame inhibition by 2-BTP.

## Modeling Results and Discussion

The full mechanism was used to study the effects of the agent 2-BTP on premixed methane-air flames. In the modeling, we employed simulations with a range of different methane-air stoichiometries, different agents, and a range of agent loadings. We employed the graphics post-processor XSenkplot<sup>11</sup> to conduct a reaction path analysis of the results.

We found that 2-BTP was least effective for lean flames, comparable in effectiveness to CF<sub>3</sub>Br in stoichiometric flames, and more effective in rich flames. Lean methane-air flames were modeled with different agents to study the impact of heat release using 2-BTP, CF<sub>3</sub>Br (bromotrifluoromethane), and C<sub>2</sub>HF<sub>5</sub> (pentafluoroethane). The addition of C<sub>2</sub>HF<sub>5</sub> to lean flames was found to increase the burning velocity (lowering the flammability limit), while for CF<sub>3</sub>Br significant inhibition was observed. Inhibition by 2-BTP in lean flames was low with an increase in the flame temperature observed.

The competition between inhibition by 2-BTP and increasing flammability is largely the completion between inhibition by Br atoms and heat release by the combustion of CF<sub>3</sub> and other non-bromine-containing intermediates. 2-BTP decomposes rapidly in the flame forming bromine-containing species resulting in catalytic reduction of radicals in the flame. In lean flames, the increase in flame temperatures due to heat release increases the radical concentration beyond the ability of the bromine-driven radical catalytic cycle to suppress the flame chemistry.

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