Influence of Antimony-Halogen Additives on Flame Propagation

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Abstract

A kinetic model for flame inhibition by antimony-halogen compounds in hydrocarbon flames is developed. Thermodynamic data for the relevant species are assembled from the literature, and calculations are performed for a large set of additional species of Sb-Br-C-H-O system. The main Sb- and Br-containing species in the combustion products and reaction zone are determined using flame equilibrium calculations with a set of possible Sb-Br-C-H-O species, and these are used to develop the species and reactions in a detailed kinetic model for antimony flame inhibition. The complete thermodynamic data set and kinetic mechanism are presented. Laminar burning velocity simulations are used to validate the mechanism against available data in the literature, as well as to explore the relative performance of the antimony-halogen compounds. Further analysis of the premixed flame simulations has unraveled the catalytic radical recombination cycle of antimony. It includes (primarily) the species Sb, SbO, SbO_2, and HOSbO, and the reactions: $Sb+O+M=SbO+M$; $Sb+O_2+M=SbO_2+M$; $SbO+H=Sb+OH$; $SbO+O=Sb+O_2$; $SbO+OH+M=HOSbO+M$; $SbO_2+H_2O=HOSbO+OH$; $HOSbO+H=SbO+H_2O$; $SbO+O+M=SbO_2+M$. The inhibition cycles of antimony are shown to be more effective than those of bromine, and intermediate between the highly effective agents CF_3Br and trimethylphosphate. Preliminary examination of a Sb/Br gas-phase system did not show synergism in the gas-phase catalytic cycles (i.e., they acted essentially independently).

Keywords: antimony fire retardant, bromine fire retardant, synergism, flame inhibition, antimony tribromide

1. Introduction

Antimony trioxide, together with organochlorine and organobromine compounds, is a widely used fire retardant additive in commodity polymers. This application represents the largest commercial use of antimony (as well as of bromine). The fire retardant action is believed to occur in the gas phase (Fenimore and Martin, 1966b, Fenimore and Martin, 1966a, Fenimore and Jones, 1966, Fenimore and Martin, 1972). Yet in spite of the long use and many studies of antimony-bromine systems as fire retardants, for example (Hastie and McBee, 1975, Khalturinskii and Rudakova, 2008, Lewin, 1999, Lewin, 2001, Linteris, 2002, Salmeia et al., 2015, Weil, 2011, Weil and Levchik, 2007), there have been few fundamental studies describing the gas phase inhibition mechanism by antimony and its synergetic effect when combined with chlorine or bromine. Unlike most other gas-phase active flame inhibitors, there are no kinetic or thermodynamic models for antimony flame inhibition, and consequently, there has been no simulation or analysis of those systems. Due to health, environmental, and other concerns, there is motivation in industry to find

alternatives to the antimony-bromine system for fire retarding high-volume commodity polymers. It is believed that a detailed understanding of the flame inhibition mechanism of the antimony-bromine system will allow more efficient use of existing and new formulations, as well as development of alternative compounds.

There have been a few experimental studies of the inhibition effectiveness of antimony compounds for gas phase flames. In seminal work, Lask and Wagner (Lask and Wagner, 1962) examined the reduction in laminar burning velocity (using nozzle burners) and flammability limits with addition of a wide variety of compounds (including the elements: P, Br, Cl, Ti, Sn, Ge, Fe) to premixed hexane- and hydrogen-air flames. In related unpublished work (as cited in (McHale, 1969)) they did measurements with $SbCl_3$ and found it to be about 15 % less effective than the highly effective agents $SnCl_4$, $TiCl_4$, and $POCl_3$, which, based on experiments in premixed methane-air flames for $SnCl_4$ and CF_3Br (Linteris et al., 2002), implies that $SbCl_3$ is about 2.6 times as effective as CF_3Br. Miller et al. (Miller et al., 1963) studied the influence of antimony pentachloride on hydrogen-air burning velocities, and found it to be about five times as effective as CF_3Br for rich flames. In molecular-beam mass spectrometry experiments, Hastie et al. (Hastie, 1973a, Hastie, 1973b, Hastie and McBee, 1975) determined the flame structure of methane-air flames inhibited by $SbCl_3$ and $SbBr_3$. All these studies demonstrated that antimony compounds themselves are effective flame inhibitors.

The goal of the present work is to develop a kinetic model of flame inhibition by antimony-bromine compounds and use it to study the influence of Sb-Br compounds on premixed flames. To this end we have performed calculations of thermodynamic properties for a large set Sb-Br-C-H-O species, and use these in combustion equilibrium calculations for methane-air flames doped by Sb- and Br-containing additives. Based on these calculations and the experimental results for similar systems in the literature, a limited set of relevant species is suggested for initial kinetic model generation. This model is used to simulate the influence of several Sb-containing compounds (SbH_3, $SbCl_3$, $SbCl_5$, $SbBr_3$, ClSbO, BrSbO) on the burning velocity of methane-air flames; for comparison, data for the inhibition effectiveness of bromine- (HBr) and phosphorus-containing (TMP, trimethyl phosphate) additives are also presented. The mechanism of inhibition by antimony compounds is studied; and finally, a simple binary system with Sb- and Br-containing species is simulated to explore synergism in the gas phase.

2. Kinetic models and modeling procedure

Although it is most desirable to test the Sb flame inhibition model using data for a simple Sb-containing hydrocarbon, there are no such data in the literature for comparison. Data only exist for H_2-air flames inhibited by $SbCl_5$ (Miller et al., 1963) and hexane-air flames inhibited by $SbCl_3$ (McHale, 1969). Hence, in order to test the Sb mechanism against experimental data, kinetic models are required for Sb/Cl flame inhibition in hydrocarbon-air flames (hydrogen-air, hexane-air), as well as for the combined Sb/Br flame inhibition (present work), and methane-air flames (for exploratory simulations). In total, the inhibiting species of interest (for which mechanisms are required) in the present work are: SbH_3, $SbBr_3$, BrSbO, $SbCl_3$, $SbCl_5$, ClSbO, Sb_4O_6, CF_3Br, HBr and TMP (trimethyl phosphate). The sources of these required models are described below.

For methane and hydrogen flames, the kinetic model Grimech-3.0 is employed (Smith et al., 2000). For hexane, the C1–C4 model of Wang et al (Wang et al., 2007) is used as a basis, as in our previous work (Babushok et al., 2012), with the work of Burcat et al. (Burcat et al., 1996) providing decomposition pathways down to C1-C4 species. The bromine-species reactions (Br-C-H-O) are extracted from a recently-developed mechanism for $C_3H_2F_3Br$ flame inhibition (Babushok et al., 2015). The chlorine-species reactions (Cl-C-H-O) are extracted from recent work for $C_2HF_3Cl_2$ flame inhibition (Babushok et al., 2014). Since P and Sb are in the same periodic group, simulations with a phosphorus compound are useful for comparison. Trimethylphosphate (TMP) is used for these comparisons, since experimental, modeling, and validation studies have been performed for it. To model phosphorus-species flame inhibition by TMP, the kinetic model of Jayavera et al. is used (Jayaweera et al., 2005). Development of the kinetic model for antimony-bromine compounds is described below.

Note that Sb_4O_6, antimony oxide, is used as a model compound for test calculations and for comparison purposes. Sb_4O_6 is a product of antimony combustion in air for a low temperature range. It is known that evaporation of antimony trioxide, Sb_2O_3 leads to Sb_4O_6 in a gas phase (Asryan et al., 2004, Behrens and Rosenbla.Gm, 1973, Kunkel et al., 2014). The kinetics of the decomposition of Sb_4O_6 in the flame is represented by a simplified, overall reaction down to the Sb-containing species considered in the kinetic model. It is assumed that the decomposition details have a relatively small impact on the burning velocity of inhibited flames, as discussed previously (Linteris et al., 2000). The Chemkin set of programs of Sandia Laboratory is used for the

combustion equilibrium calculations and for modeling laminar premix flames. Typical values of grad and curve parameters are 0.12 and 0.27, respectively, for the calculations.

3. Results and Discussion

3.1. Sb-, Br-, and Cl-containing species list and thermochemical data

A starting list of compounds for inclusion in the model was developed from consideration of possible antimony species containing Br, Cl, H, C, and O. Resources for this list include the CAS registry (SciFinder) and thermodynamic databases (Goos et al., 2012, Gurvich et al., 1993). Further refinement was performed based on calculated thermodynamic data (Skulan et al., 2006), analogy with the phosphorus flame inhibition model (Jayaweera et al., 2005), mass-spectrometry (Hastie, 1973a, Hastie, 1973b, Hastie et al., 1986, Hastie and McBee, 1975) and spectroscopic (Farber and Srivastava, 1975) species measurement in flames, and other species observed experimentally. The list is presented in **Error! Reference source not found.**. In this initial mechanism, the list was constrained to species with one antimony atom (assuming that in flame reaction zone, the antimony species will have decomposed to those with only one Sb atom). As described below, thermodynamic calculations indicate a relatively high concentration of Sb atom at equilibrium; therefore, some recombination of Sb atoms can be expected and the species Sb_2 was included.

As indicated in **Error! Reference source not found.**, thermodynamic data were obtained or calculated for the heat of formation ΔH_f, entropy S, and specific heat C_p at 298 K. Literature data from Burcat et al. (Goos et al., 2012), Skulan et al. (Skulan et al., 2006) and the IVTANTHERMO database (Gurvich et al., 1993) were used when available. For the remaining species of interest, thermodynamic data were calculated at the CCSD(T)/aug-cc-pVTZ level of theory based on structures optimized at the BP86/SV(P) level as implemented in the program package TURBOMOLE (Ahlrichs et al., 1989). This was done using standard protocols for thermodynamic function calculations like rigid rotor and harmonic oscillator. Consideration of relativistic effects by ECP (as implemented in TURBOMOLE) was performed (with no spin-orbit coupling). Based on the calculated properties, data in CHEMKIN format (polynomials) were generated, as presented in the Supplementary Materials.

3.2. Flame equilibrium calculations

In order to estimate the relative potential contribution of the different species in **Error! Reference source not found.** at flame temperatures, combustion equilibrium calculations were performed (constant pressure, constant enthalpy or temperature) using the Sandia EQUIL program (Reynolds, 1986). The initial conditions are methane-air mixtures at 298 K, 1 bar, to which the antimony compound (SbH_3, $SbBr_3$) is added at a volume fraction (in the entire mixture) of 0.25 %. For the additive SbH_3, Figure 1 shows the equilibrium volume fraction for each of the species in **Error! Reference source not found.** (for those having a peak value above 10^{-11}) as a function of temperature. Figure 2 shows the results for $SbBr_3$ addition as a function of combustion temperature, while Figure 3 shows the results as a function of the initial equivalence ratio of the methane-air flame. As Figure 1 and Figure 3 show, the main Sb-containing species, in approximate order of relative abundance, are HOSbO, Sb, SbO, $Sb(OH)_3$, $Sb(OH)_2$, SbOH, SbH, HSbO, SbO_2, and $HOSbO_2$. To determine the influence of agent loading on equilibrium product distribution, calculations (not shown here) were also performed varying the initial antimony species (in this case, SbH_3) volume fraction from 0.1 to 3 %. The results show an approximate linear increase in all product species concentrations, with no major changes in the product distributions. For $SbBr_3$ addition (also at a volume fraction of 0.25 %), Figure 2 shows that the major equilibrium species in the methane-air flame are: HBr, Br, HOSbO, BrSbO, Sb, SbO, (OH)2SbBr, Br_2, (HO)SbBr, SbBr, BrOH, BrO, SbBr3, SbBr2, and $(OH)SbBr_2$. Based on these equilibrium calculations and the results for the similar phosphorus inhibition mechanism, the following species were adopted for the first iteration of the kinetic model of antimony species: Sb, SbO, SbO_2, SbO_3, HOSbO, $HOSbO_2$, Sb_2, SbOH, and SbH. To model the behavior of $SbBr_3$, $SbCl_3$ and $SbCl_5$ the following species were additionally included: $SbBr_3$, $SbBr_2$, $SbCl_5$, $SbCl_4$, $SbCl_3$, $SbCl_2$,SbCl, ClSbO, SbBr, and BrSbO.

The present equilibrium calculations for antimony-containing species can be compared with similar calculation for phosphorus-containing compounds. For the antimony system, the results show a high concentration of Sb atoms, while SbO and HOSbO dominate as the main oxygenated antimony species. This is in a contrast to phosphorus-containing inhibitors for which the dominant gas-phase oxygenated species are PO_2, HOPO and $HOPO_2$, and P atom is not important. The equilibrium concentration of $HOSbO_2$ is substantially less than HOSbO implying that inhibition chemistry should be dominated by the HOSbO species. This is the opposite of

phosphorus inhibition chemistry where both HOPO and $HOPO_2$ species are important, and participate in two scavenging cycles: PO_2 < = > HOPO and PO_2 < = >$HOPO_2$.

Note that experimental results (Farber and Srivastava, 1975, Hastie, 1973a) detected Sb atom, SbO, $HOSbO_2$, $OSb(OH)_3$ and Sb_4O_6 in the flame reaction zone and combustion products of methane-air and hydrogen-air flames. The species Sb_4O_6 species was observed in the preheat zone of a methane-air flame (Hastie, 1973a). We believe that the significant concentrations of $OSb(OH)_3$ and $HOSbO_2$ observed in the experiments of Farber and Srivastava (Farber and Srivastava, 1975) are the result of post-flame reactions during the quenching process with the additional mixing with the surrounding air.

3.3. Kinetic model of inhibition by antimony-containing compounds

To our knowledge there are no available gas phase kinetic models which include Sb-chemistry, and a review of the literature shows that elementary rate data for reactions of Sb-containing stable species and radicals are practically absent. A list of plausible reactions with Sb-, Br- and Cl-containing species was considered. They include the decomposition reactions of SbH_3, $SbBr_3$, $SbCl_3$ and $SbCl_5$, reactions of HOSbO, $HOSbO_2$, BrSbO and ClSbO and its products (Sb, SbO, SbO_2, SBO_3, SbH, SbH_2,SbOH, SbBr, $SbBr_2$, Sb_2) with the important radicals (H, OH, O, Br, Cl, CH_3, HCO, HO_2), the main hydrocarbon species (CH_4, C_2H_6, CH_2O), and with the bromine- and chlorine-containing species. Based on thermochemical considerations and estimation of species equilibrium concentrations, this list was reduced to that in Table 2. It contains 179 reactions with 16 Sb/Br-containing species (Sb-Br system), which are combined with the Grimech 3.0 model for methane oxidation, and the CF_3Br flame inhibition kinetic model (Babushok et al., 2015) for the bromine-species part of the mechanism. The antimony-chlorine kinetic sub-model is presented in the Supplemental Material. Most of the rate constants are estimated based on analogy and using empirical correlations.

As a first step for validating a kinetic mechanism, it is useful to have burning velocity data for inhibited flames for comparison with calculated values. Unfortunately, despite the widespread use of antimony as a fire retardant, there are practically no available experimental data on the effects of Sb-C-H-O compounds on air/hydrocarbon flames for comparison with model predictions. As described above, Miller et al. have provided experimental data (intended for screening purposes)(Miller et al., 1963), of the effect of numerous flame inhibitors on the burning

velocity of hydrogen-air flames measured using the total area method with conical premixed flame (Andrews and Bradley, 1972). Using their data, Figure 4 shows the measured and predicted burning velocity of a hydrogen-air flame (298 K, 1 bar, equivalence ratio of 1.75) with added $SbCl_5$. Although there is large scatter in the experimental data, the agreement appears to be reasonable. Other available data include the unpublished work of Lask and Wagner (cited in (McHale, 1969)) described above, for stoichiometric premixed n-hexane-air flames (modelled as 298 K, 1 bar) with added $SbCl_3$. As with the other inhibitors of the study, the data are reported as the quantity of $SbCl_3$ required to reduce the burning velocity of the flames by 30 %. The numerically calculated volume fraction for this level of flame inhibition is 0.18 %, which compares reasonably well to the experimental value (0.22 %).

3.4. Burning velocity simulations, mechanism of flame inhibition by antimony

The influence of inhibitor concentration on the burning velocity of laminar hydrocarbon-air flames is often used as a metric for flame inhibition effectiveness. For comparison purposes, Figure 5 shows the calculated burning velocity of stoichiometric methane-air flames with added SbH_3, $SbBr_3$, $SbCl_3$, Sb_4O_6, BrSbO, and ClSbO, as well as for the more thoroughly studied (and validated) agents CF_3Br, HBr and TMP ($PO(OCH_3)_3$). Using the current mechanism, SbH_3 is less effective than the phosphorus compound (TMP), but more effective than bromine containing compounds. As with most flame inhibitors, the marginal reduction in burning velocity decreases as the volume fraction of agent increases (saturation of the inhibition effect (Noto et al., 1998)). At relatively small additive concentrations, the burning velocity reductions of different antimony compounds are relatively close to each other, and close to that of antimony itself (for which data are not shown, but which is the most effective moiety of antimony compounds). Addition of Br atoms to the antimony-containing compound increases the inhibition effectiveness significantly, proportional to the number of Br atoms; Cl addition provides a significant but smaller effect, consistent with previous findings for halogen inhibition (Dixon-Lewis and Simpson, 1977, Westbrook, 1982, Babushok and Tsang, 2000). With the present kinetic mechanism, the modeling results show that for a 10 % reduction in burning velocity (a common metric), Sb-containing compounds (e.g., Sb_4O_6) are approximately 3 and 4.3 times more effective than CF_3Br and HBr, respectively.

For a methane-air flame with SbH_3 added at a volume fraction of 0.2 %, Figure 6 shows the volume fractions of major species of interest as a function of position in flame. Concentrations of the species SbH_2 and SbH, which are intermediates during decomposition of SbH_3, are small as a result of their high reactivity. The species HOSbO is present at the highest volume fraction in the flame (around 0.001), existing at super equilibrium levels in the preheat zone, and then approaches equilibrium. The species SbO forms slightly later in the preheat zone, is also present at super-equilibrium levels (about 10x), and then decays towards equilibrium concentrations. The species Sb forms still later, and is sub-equilibrium throughout. The dips in the concentrations of these species at the location of peak radical concentration (flame coordinate of 0.05 cm to 0.1 cm) are related to their consumption in the catalytic radical recombination cycles described below. The volume fraction of another important species in the cycle, SbO_2, is approximately one to two orders of magnitude smaller than that of SbO as a result of relatively high rates of its conversion to HOSbO.

Figure 7 shows the reaction pathways of SbH_3 decomposition and the fate of antimony species in the flame reaction zone. In the figure, arrows connect the reactants and products of a reaction; the species next to the arrow is the reaction partner, and the number adjacent is the fraction (in %) of the overall consumption rate of the first reactant in that reaction. No reaction partner denotes a unimolecular decomposition reaction; no fraction indicates nearly all of the species goes through that reaction pathway. SbH_3 is consumed primarily through a decomposition reaction, and also via its reaction with radicals (H, OH), to form SbH_2. The SbH_2 radical and its product, SbH, are mostly consumed through decomposition reactions and via reactions with radicals, forming Sb atom at the end of decomposition sequence. The Sb atom, along with the other intermediate species SbO, SbO_2 and HOSbO, form the sequence of reactions depicted in Figure 7:

$$Sb+O+M=SbO+M \quad (1)$$

$$Sb+O_2+M=SbO_2+M \quad (2)$$

$$SbO+O+M=SbO_2+M \quad (3)$$

$$SbO+H=Sb+OH \quad (4)$$

$$SbO+O=Sb+O_2 \quad (5)$$

$$SbO+OH+M=HOSbO+M \quad (6)$$

$$SbO_2+H_2=HOSbO+H \quad (7)$$

$$SbO_2+H_2O=HOSbO+OH \quad (8)$$

$$HOSbO+H=SbO+H_2O \quad (9)$$

As the figure shows, there are multiple catalytic radical scavenging cycles. The simplest is the binary cycle Sb ⇔ SbO via reactions (1), (4), and (5), while a similar cycle SbO ⇔ HOSbO via reactions (6) and (9) also plays a role. The next is more complicated: Sb atom reacts to form SbO_2 (via reaction (2) or reactions (1) followed by (3). Reactions of SbO_2 with H_2 and H_2O lead to the formation of antimonic acid (HOSbO). The reaction of HOSbO with hydrogen atom (9) leads to SbO and H_2O and completes the second cycle.

For the present conditions (stoichiometric methane flame with initial SbH_3 volume fraction of 0.25 %) the first cycle is about 30 % as important of the second cycle (based on the Sb-atom consumption rates). A rough estimate of the regeneration coefficient (the number of radicals recombined per molecule of active catalytic species) (Noto et al., 1998) shows that it is in the range of 15 to 25 (depending on agent concentration and conditions). This value reflects a higher inhibition effectiveness of antimony-containing compounds in comparison with CF_3Br, which has an estimated regeneration coefficient between 5 and 7 (Noto et al., 1998).

The antimony catalytic cycles of Figure 7 can be compared to those of phosphorous (e.g., DMMP (Babushok and Tsang, 1999, Jayaweera et al., 2005). With antimony, reactions of Sb atom are important, whereas those of P are not; reactions of $HOSbO_2$ are not important, but those of $HOPO_2$ are, particularly for lean conditions. Also, reactions of SbO are important contributors to radical scavenging cycles, but those of PO are not. The relative ratios of [PO]:[PO_2]and [SbO]:[SbO_2] are also different: for the antimony system, [SbO_2] << [SbO] (by about 100 times), but for the phosphorus system, they are roughly of the same order of magnitude.

3.5. Antimony-bromine gas-phase synergism

The combination of antimony trioxide with a chlorinated or brominated species in polymers is empirically known to be a synergistic fire retardant mixture for polymers. Hence, it is of interest to explore if the present model shows any synergism in the gas-phase inhibition mechanism of a system with both Sb and Br present. To this end, the laminar burning velocity of a stoichiometric methane-air flame was calculated with an additive composed of varying levels of SbH_3 and HBr. The total additive volume fraction was fixed at either of 0.1 % or 0.2 %, and the fraction of SbH_3 in the inhibitor was varied from 100 % to 0 % (with the rest HBr). Figure 8 shows the calculated burning velocity as a function of volume fraction of HBr in the total mix (total

inhibitor volume fraction of the blend is constant at 0.1 % or 0.2 %). (For reference, the uninhibited burning velocity is 37.5 cm/s). At X_{HBr} = 0 (X_{SbH3}=0.001 or 0.002), the decrease in burning velocity due to the additive is at a maximum value. Replacement of SbH_3 by HBr leads to a lower decrease of burning velocity (i.e., SbH_3 is a more effective inhibitor than HBr). A linear dependence of burning velocity with HBr volume fraction (dotted lines in Figure 8) indicates a lack of synergism (i.e., the total inhibition is a sum of the inhibition from each component of the blend); curves falling below the dotted line indicate synergism, with some interaction of inhibitors leading an increased effect.

From Figure 8, it can be seen that the SbH_3/HBr blend has a nearly linear dependence on fraction of HBr in the blend, with a slight synergism, that increases as the loading of the inhibitor increases (from 0.1 % to 0.2 % volume fraction). Nonetheless, the synergetic effect indicated by these calculations is small. Reaction rate analysis demonstrates that reaction rates of species containing both Sb and Br are small in comparison to the reaction rates of the main reactions of antimony and bromine inhibition cycles. For example, the flux of radical consumption through reactions of BrSbO is more than two orders of magnitude smaller than that caused by reactions of HOSBO, SbO, HBr or Br; reaction fluxes for SbBr species are even smaller, by another order of magnitude. Moreover, a detailed analysis of possible additional Sb-Br-containing species and "cross-interaction" reactions did not reveal additional reactions which might have substantial contribution to the gas flame inhibition chemistry.

It is of interest that combining effective moieties (e.g., Br and Sb) in a single molecule actually reduces the availability of one of the moieties to participate in its own inhibition cycles. Hence, in order to show synergism, the combined species would have to have a particularly effective catalytic cycle to compensate for the loss of the cycle of one of the elements.

The above analysis for synergism is limited to the ideal case of two effective inhibitors already present in the gas phase, and explores the possibility of synergism in radical recombination cycles. Nonetheless, actual fire retarded polymers have many other physical and chemical processes in which synergistic action may be occurring. These include polymer and fire retardant decomposition rates (and timing), char formation, transport of the active species to gas phase, and interactions of the resultant flame (and its heat release) with the fuel decomposition (i.e., fuel generation) processes. While examination of these processes is beyond the scope of the present work, the availability of a validated gas-phase kinetic model for flame inhibition by antimony and

bromine can clearly help to distinguish between fire retardant mechanisms and synergistic effects for specific physical and chemical systems of interest.

As one example of the type of information that might prove to be useful, examination of the kinetics of antimony-inhibited flames has indicated that the species Sb_4O_6 may play an unexpected role. In the polymer industry, antimony trioxide (Sb_2O_3) is typically used as a fire retardant additive (as a synergist with brominated compounds). Since Sb_2O_3 has a relatively high boiling point, 1425 ^oC (melting point, 655 ^oC), antimony may be transported to the gas-phase via antimony trihalides or antimony oxyhalides (resulting from reaction of Sb_2O_3 with halogenated species in the condensed phase) (Hastie, 1973a, Hastie and McBee, 1975). Nonetheless, Sb_2O_3 likely forms as an intermediate species in the gas phase, and experimental measurements show that Sb_2O_3 then forms Sb_4O_6 as a main antimony compound in the gas phase (Asryan et al., 2004, Behrens and Rosenbla.Gm, 1973, Kunkel et al., 2014). Preliminary flame equilibrium estimates (using thermochemistry of Sb_4O_6 from (Gurvich et al., 1993)) demonstrate that this compound is rather stable at high temperatures, and may survive in a combustion atmosphere up to 1400 K to 1700 K. This high stability of Sb_4O_6 in the gas phase should lead to the delay in formation of the species active in the catalytic cycle (Sb, SbO, SbO_2 and HOSbO), and hence delay of inhibition processes. While rudimentary reactions for the formation and consumption of the species Sb_4O_6 are not in the present mechanism, its formation may play an important role in the effectiveness of antimony compounds as gas-phase fire retardants. Moreover, since the condensation process is strongly influenced by the time-temperature history in the flowfield of the relevant flame (i.e., fire) (Rumminger and Linteris, 2002), any sequestration of the active Sb compounds to Sb_4O_6 may be strongly affected by the particular flame structure of the test method, fire, or polymer of interest.

4. Conclusions

The present work has developed the first detailed kinetic model for gas-phase flame inhibition by antimony compounds, as well as ones for antimony/chlorine and antimony/bromine systems. These models can serve as the basis for further development, testing, and refinement. The first steps at model validation were made using available data from literature, and the model was applied via premixed flame speed simulations to gain insight into gas-phase flame inhibition by antimony/halogen compounds. The main results of the present study are:

1) Thermochemical data for the relevant species of Sb-Br-Cl-H-C-O compounds in flame environments were assembled from the literature; when needed data were missing, they were calculated. These data provide a basis for flame inhibition models by Sb-, Cl-, and Br-containing compounds.

2) Combustion equilibrium calculations were performed to determine the main antimony-bromine species in combustion products and in a flame reaction zone. Calculations were performed for species distribution as a function of combustion temperature, equivalence ratio, and inhibitor loading for representative compounds (SbH_3 and $SbBr_3$) in a methane/air flame.

3) Based on the equilibrium calculation results and other considerations, a limited set of species was developed for inclusion in the kinetic model for flames inhibition. These include: Sb, SbO, SbO_2, SbO_3, HOSbO, $HOSbO_2$, SbH, SbOH, Sb_2, BrSbO, SbBr, $SbBr_2$, $SbBr_3$, SbH_3 and SbH_2. The reactions of the major species and radicals of hydrocarbon flames with these antimony/halogen-containing species were considered. The antimony/halogen sub-kinetic model was combined with Grimech-3.0 for methane-air flames, and included the bromine-species reactions from a flame inhibition model for CF_3Br.

4) To explore the model performance and relative efficiency of antimony/halogen systems, the burning velocity of methane-air flames was calculated for addition of SbH_3, $SbBr_3$, $SbCl_3$, Sb_4O_6, BrSbO and ClSbO, and the results compared to other well-studied flame inhibitors (HBr, CF_3Br and trimethylphosphate). The results indicate that the performance of the antimony compounds is intermediate between compounds of bromine and phosphorus compounds (e.g., CF_3Br, TMP). As was expected, $SbBr_3$ is more effective than $SbCl_3$ and SbH_3, and BrSbO is more effective than ClSbO.

5) For the antimony-inhibited premixed flames, reaction pathway analysis revealed the radical scavenging sequences. The catalytic radical recombination sequences include the species: Sb, SbO, SbO_2 and HOSbO (in contrast to the phosphorus catalytic cycles that are dominated by HOPO, $HOPO_2$, PO_2 and PO).

6) Analysis of methane-air flame inhibition by a model Sb/Br combination (SbH_3-HBr) did not show synergism in the gas phase; i.e., the inhibition chemistry of the Sb and Br cycles were relatively independent.

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Table 1 - Thermodynamic data of antimony-containing species (1 bar).

Species	Reaction used for calculations	ΔH_f [kJ/mol]	S [J/mol/K]	C_p [J/mol/K]	Reference
Sb		264.6	180.3	20.79	(Goos et al., 2012)
Sb_2		236	255.9	36.41	(Goos et al., 2012)
SbH		246.4	215.9	29.2	(Skulan et al., 2006)
SbH_2		207.4	234.3	35.92	(Goos et al., 2012)
SbH_3		144.8	232.7	41.22	(Goos et al., 2012)
SbCl		94.5	257.3	35.93	(Skulan et al., 2006)
$SbCl_2$		-98.7	280.8	43.23	(Goos et al., 2012)
$SbCl_3$		-313.4	341.1	77.39	(Goos et al., 2012)
$SbCl_4$		-290.8	407.8	94.26	(Skulan et al., 2006), est
$SbCl_5$		-433.0	422.2	122.1	(Goos et al., 2012)
ClSbO		-106.7	299.8	50.83	(Hastie and McBee, 1975), est
SbO	$SbH_3 + 1.25O_2 = SbO + 1.5\ H_2O$	+137.6	244.4	32.01	This work
HSbO	$SbH_3 + O_2 = HSbO + H_2O$	+90.2	267.8	40.11	This work
Sb(OH)	$SbH_3 + O_2 = Sb(OH) + H_2O$	+43.7	264.4	40.54	This work
HOSbH		-15.5	278.1	50.77	(Skulan et al., 2006)
$OSbH_2$		185.8	272.7	49.51	(Skulan et al., 2006)
$HOSbH_2$		-75.7	274.6	58.56	(Skulan et al., 2006)
SbO_2	$SbH_3 + 1.75O_2 = SbO_2 + 1.5\ H_2O$	+29.3	293.4	48.52	This work
$HSbO_2$	$SbH_3 + 1.5\ O_2 = HSbO_2 + H_2O$	+18.7	302.4	57.83	This work
(HO)SbO	$SbH_3 + 1.5\ O_2 = (HO)SbO + H_2O$	-233.8	302.6	56.24	This work
(HO)HSbO	$SbH_3 + 1.25\ O_2 = (HO)HSbO + 0.5\ H_2O$	-112.3	313.5	69.88	This work
$Sb(OH)_2$	$SbH_3 + 1.25\ O_2 = Sb(OH)_2 + 0.5\ H_2O$	-283.8	325.1	70.74	This work
$(HO)_2SbH$		-339.3	308.9	75.69	(Skulan et al., 2006)
SbO_3	$SbH_3 + 2.25O_2 = SbO_3 + 1.5\ H_2O$	+99.0	336.6	69.39	This work

$(HO)SbO_2$	$SbH_3 + 2\ O_2 = (HO)SbO_2 + H_2O$	-252.7	336.9	75.21	This work
$(HO)_2HSbO$	$SbH_3 + 1.5\ O_2 = (HO)_2HSbO$	-458.8	348.6	95.22	This work
$Sb(OH)_3$	$SbH_3 + 1.5\ O_2 = Sb(OH)_3$	-664.0	347.2	98.49	This work
$(HO)_2SbO_2$	$SbH_3 + 2.25\ O_2 = (HO)_2SbO_2 + 0.5\ H_2O$	-418.8	388.9	108.62	This work
$(HO)_3SbO$	$SbH_3 + 2\ O_2 = (HO)_3SbO$	-718.4	386.3	116.12	This work
SbBr	$SbH_3 + HBr + O_2 = SbBr + 2\ H_2O$	+185.8	268.6	36.51	This work
HSbBr	$SbH_3 + HBr + 0.75\ O_2 = HSbBr + 1.5\ H_2O$	+131.9	292.5	45.29	This work
H_2SbBr	$SbH_3 + HBr + 0.5\ O_2 = H_2SbBr + H_2O$	+60.3	296.1	52.58	This work
BrSbO	$SbH_3 + HBr + 1.5\ O_2 = BrSbO + 2\ H_2O$	-54.9	322.8	51.42	This work
(HO)SbBr	$SbH_3 + HBr + 1.25\ O_2 = (HO)SbBr + 1.5\ H_2O$	-129.4	334.5	63.56	This work
$BrSbO_2$	$SbH_3 + HBr + 2\ O_2 = BrSbO_2 + 2\ H_2O$	-73.4	350.9	70.19	This work
(HO)BrSbO	$SbH_3 + HBr + 1.75\ O_2 = (HO)BrSbO + 1.5\ H_2O$	-213.3	370.7	83.62	This work
$(HO)_2SbBr$	$SbH_3 + HBr + 1.5\ O_2 = (HO)_2SbBr + H_2O$	-495.0	372.9	92.60	This work
$(HO)_2BrSbO$	$SbH_3 + HBr + 2\ O_2 = (HO)_2BrSbO + H_2O$	-536.7	408.0	111.29	This work
$SbBr_2$	$SbH_3 + 2\ HBr + 1.25\ O_2 = SbBr_2 + 2.5\ H_2O$	+29.8	341.6	56.39	This work
$HSbBr_2$	$SbH_3 + 2\ HBr + O_2 = HSbBr_2 + 2\ H_2O$	-35.0	349.7	65.64	This work
Br_2SbO	$SbH_3 + 2\ HBr + 1.75\ O_2 = Br_2SbO + 2.5\ H_2O$	-44.0	383.2	76.75	This work
$(HO)SbBr_2$	$SbH_3 + 2\ HBr + 1.5\ O_2 = (HO)SbBr_2 + 2\ H_2O$	-320.4	387.7	86.79	This work
$SbBr_3$	$SbH_3 + 3\ HBr + 1.5\ O_2 = SbBr_3 + 3\ H_2O$	-139.9	393.4	80.33	This work
Br_3SbO	$SbH_3 + 3\ HBr + 2\ O_2 = Br_3SbO + 3\ H_2O$	-175.8	422.4	98.89	This work
CH_3SbO_2	$SbH_3 + CH_4 + 2\ O_2 = CH_3SbO_2 + 2\ H_2O$	-51.8	363.2	84.12	This work
$(CH_3O)SbO$	$SbH_3 + CH_4 + 2\ O_2 = (CH_3O)SbO + 2\ H_2O$	-202.0	342.9	76.68	This work
$(CH_3O)SbO_2$	$SbH_3 + CH_4 + 2.5\ O_2 = (CH_3O)SbO_2 + 2\ H_2O$	-219.8	348.1	96.03	This work
CH_3SbBr	$SbH_3+CH_4+HBr+1.25O_2 = CH_3SbBr + 2.5\ H_2O$	+82.0	342.7	70.78	This work
CH_3SbBr_2	$SbH_3+CH_4+2HBr+1.5O_2 = CH_3SbBr_2 + 3\ H_2O$	-100.6	395.1	94.00	This work
$(HO)(CH_3)SbBr$	$SbH_3+CH_4+HBr+1.5O_2=(HO)CH_3SbBr+2H_2O$	-264.5	380.1	99.49	This work
$(CH_3)_2SbBr$	$SbH_3+2CH_4+HBr+1.5O_2=(CH_3)_2SbBr+3H_2O$	-48.0	388.8	107.63	This work
$Sb(CH_3)$		217.1	273.5	46.81	(Skulan et al., 2006)
$Sb(CH_3)_2$		143.93	326.2	78.06	(Goos et al., 2012)
$Sb(CH_3)_3$		38.5	361.1	111.0	(Goos et al., 2012)
$SbH(CH_3)$		177.8	286.4	55.86	(Skulan et al., 2006)
SbH_2CH_3		114.2	285.9	63.12	(Skulan et al., 2006)
$SbH(CH_3)_2$		78.7	329.2	86.85	(Skulan et al., 2006)
$Sb(CH_3)(OH)$		-59.8	324.1	72.32	(Skulan et al., 2006)
$SB(CH_3)_2(OH)$		-169.5	366.4	107.38	(Skulan et al., 2006)
$SB(CH_3)(OH)_2$		-394.1	353.2	103.19	(Skulan et al., 2006)

$SB(H)_2CH_2$		323.4	294.6	63.61	(Skulan et al., 2006)
Sb_4O_6		-1222.3	462.3	188.84	(Gurvich et al., 1993)

Table 2 - Kinetic model for antimony/bromine containing species (units: mole,s,cm,kJ).

No	Reaction	A	n	E
1.	H+SBO=SB+OH	2.70E+13	0	31.38
2.	SBO+OH+M=HOSBO+M H2O/16/ H2/2.5/	4.00E+22	-2.1	6.65
3.	SBO+O+M=SBO2+M H2O/16/ H2/2.5/	4.80E+25	-2.6	7.20
4.	CH3+SBO2=CH3O+SBO	2.00E+13	0	41.84
5.	SBO+HO2=SBO2+OH	2.00E+12	0	29.29
6.	SBO+O=SB+O2	7.20E+09	1	12.55
7.	H+SBO2+M=HOSBO+M H2O/16/ H2/2.5/	4.87E+23	-2	2.70
8.	SBO2+OH+M=HOSBO2+M H2O/16/ H2/2.5/	1.60E+24	-2.3	1.19
9.	SBO2+O+M=SBO3+M H2O/16/ H2/2.5/	1.30E+27	-3.1	7.87
10.	SBO2+HCO=HOSBO+CO	1.20E+23	-3.3	9.79
11.	SBO2+HCO=CO2+SBO+H	8.40E+15	-0.8	8.08
12.	SBO2+CH2O=HCO+HOSBO	2.00E+12	0	23.01
13.	SBO2+CH4=HOSBO+CH3	3.00E+12	0	37.66
14.	SBO2+C2H6=HOSBO+C2H5	2.50E+12	0	33.47
15.	SBO2+H2O2=HO2+HOSBO	2.50E+12	0	31.38
16.	SBO2+H=OH+SBO	4.30E+13	0	29.29
17.	SBO2+O=SBO+O2	2.50E+13	0	8.37
18.	SBO3+H=SBO2+OH	6.60E+13	0	0.00
19.	SBO+SBO3=SBO2+SBO2	1.10E+13	0	4.18
20.	SBO2+HO2=O2+HOSBO	2.40E+13	0	0.00
21.	SBO3+CH3=SBO2+CH3O	2.00E+13	0	6.28
22.	SBO2+CH3O=CH2O+HOSBO	3.00E+13	0	0.00
23.	SBO2+CH3OH=HOSBO+CH3O	3.00E+12	0	37.66
24.	SBO2+CH3OH=HOSBO+CH2OH	8.00E+12	0	33.47
25.	SBO2+OH=HOSBO+O	2.40E+13	0	37.66
26.	SBO3+H+M=HOSBO2+M H2O/16/ H2/2.5/	4.80E+24	-2.4	5.98
27.	SBO3+HCO=HOSBO2+CO	3.50E+13	0	0.00
28.	SBO3+CH3O=HOSBO2+CH2O	1.80E+13	0	0.00
29.	SBO3+H2O2=HO2+HOSBO2	1.50E+12	0	14.64
30.	SBO3+OH=HOSBO2+O	6.00E+12	0	20.92
31.	SBO3+OH=HO2+SBO2	1.10E+13	0	23.01
32.	SBO3+CH2O=HOSBO2+HCO	2.50E+12	0	6.28
33.	SBO3+CH4=CH3+HOSBO2	2.00E+12	0	18.83
34.	SBO3+C2H6=C2H5+HOSBO2	3.00E+12	0	13.39
35.	SBO3+H=HOSBO+O	2.00E+12	0	4.18

36.	SBO3+H2=HOSBO2+H	1.40E+12	0	23.85
37.	SBO3+HOSBO=SBO2+HOSBO2	2.50E+12	0	18.41
38.	SBO3+O=SBO2+O2	1.80E+13	0	0.00
39.	HOSBO+O+M=HOSBO2+M H2O/16/ H2/2.5/	2.40E+27	-3	8.54
40.	HOSBO+H=H2+SBO2	2.00E+13	0	81.59
41.	HOSBO+H=H2O+SBO	3.20E+13	0	30.96
42.	HOSBO+OH=SBO2+H2O	2.40E+06	2	43.93
43.	HOSBO+O=O2+SBOH	6.50E+12	0	62.76
44.	HOSBO2+H=H2O+SBO2	1.80E+13	0	8.37
45.	HOSBO2+H=HOSBO+OH	3.80E+05	2.3	10.46
46.	HOSBO2+O=HOSBO+O2	1.60E+13	0	0.00
47.	HOSBO2+OH=H2O+SBO3	2.40E+06	2	96.23
48.	HOSBO2+OH=HOSBO+HO2	6.00E+12	0	43.93
49.	HOSBO2+O2=HO2+SBO3	7.00E+12	0	276.14
50.	HOSBO2+CH3=CH3O+HOSBO	3.00E+12	0	33.47
51.	HOSBO2+CH2=CH2O+HOSBO	4.00E+10	0	0.00
*52.	SB+O2+M=SBO2+M H2O/16/ H2/2.5/	1.16E+17	0	0.00
53.	SB+O+M=SBO+M H2O/16/ H2/2.5/	3.30E+17	0	0.00
54.	SB+SBO3=SBO+SBO2	2.00E+13	0	0.00
55.	SB+SBO2=SBO+SBO	7.00E+12	0	43.93
56.	SB+CH3O=SBO+CH3	2.50E+13	0	50.21
57.	SB+HOSBO2=SBO+HOSBO	1.50E+12	0	18.83
58.	SBH3=SBH2+H	6.60E+17	0	288.70
59.	SBH2=SBH+H	2.00E+16	0	263.59
60.	SBH3+H=SBH2+H2	4.40E+13	0	10.46
61.	SBH3+O=SBH2+OH	2.80E+13	0	10.46
62.	SBH3+OH=SBH2+H2O	1.60E+13	0	0.00
63.	SBH3+CH3=SBH2+CH4	4.00E+11	0	12.55
64.	SBH3+HCO=SBH2+CH2O	6.00E+11	0	25.10
65.	SBH2+H=SBH+H2	6.30E+13	0	4.18
66.	SBH2+O=SBH+OH	7.00E+12	0	6.28
67.	SBH2+O=SBOH+H	1.40E+13	0	4.18
68.	SBH2+OH=SBH+H2O	3.20E+11	0	0.00
69.	SBH2+HCO=SBH3+CO	8.50E+12	0	0.00
70.	SBH2+CH3=SBH+CH4	1.50E+13	0	6.28
71.	SBH2+HCO=SBH+CH2O	6.00E+11	0	20.92
72.	SBH2+SBH2=SBH3+SBH	3.00E+11	0	43.93
73.	SBH2+SB=SBH+SBH	1.50E+12	0	62.76
74.	SB+H+M=SBH+M	2.00E+16	0	0.00
75.	SBH+CH3=CH4+SB	6.70E+13	0	0.00
76.	SB+HCO=SBH+CO	8.00E+13	0	4.18

77.	SBH+O=SB+OH	3.00E+13	0	0.00
78.	SBH+H=SB+H2	5.00E+13	0	0.00
79.	SBH+OH=SB+H2O	2.00E+13	0	0.00
80.	SB+CH3O=SBH+CH2O	2.00E+13	0	8.37
81.	SBH+HCO=SB+CH2O	1.00E+13	0	14.64
82.	SB+HO2=SBH+O2	2.00E+13	0	41.84
83.	SBH+SBO2=SB+HOSBO	3.50E+12	0	0.00
84.	SBH+SBO3=SB+HOSBO2	4.00E+12	0	0.00
85.	SBH+SBH2=SBH3+SB	6.50E+11	0	39.75
86.	SB+SB+M=SB2+M	4.00E+16	0	0.00
87.	SB2+O=SBO+SB	1.00E+13	0	25.10
88.	SB2+O2=SBO+SBO	7.50E+12	0	83.68
89.	SB+SBH=SB2+H	9.00E+12	0	33.47
90.	SBO+SBH=SB2+OH	6.50E+12	0	20.92
91.	SBH+SBO2=SB2+HO2	3.00E+12	0	39.75
92.	SB+SBO2=SB2+O2	2.00E+12	0	36.40
93.	SBO+SBH=SBOH+SB	6.00E+12	0	35.98
94.	SB+OH+M=SBOH+M	4.00E+16	0	0.00
95.	SBO+HCO=SBOH+CO	3.00E+13	0	0.00
96.	SBOH+H=SBO+H2	1.00E+13	0	16.74
97.	SBOH+H=SB+H2O	2.00E+12	0	6.28
98.	SBOH+OH=SBO+H2O	7.30E+12	0	4.18
99.	SBOH+O=SBO+OH	1.50E+13	0	20.92
100.	SBOH+CH3=CH4+SBO	1.20E+13	0	18.83
101.	SBOH+HO2=SBO+H2O2	1.00E+13	0	43.10
102.	SBOH+CH3O=SBO+CH3OH	2.00E+12	0	18.41
	Sb-Br subset			
103.	BRSBO+H=HBR+SBO	3.50E+13	0	31.38
104.	BRSBO+H=SBBR+OH	3.00E+13	0	87.86
105.	BRSBO+OH=BR+HOSBO	6.00E+12	0	25.10
106.	BRSBO+OH=BROH+SBO	1.00E+13	0	96.23
107.	BRSBO+O=BR+SBO2	6.00E+12	0	33.47
108.	BRSBO+O=SBBR+O2	2.00E+13	0	46.02
109.	BRSBO+O=BRO+SBO	1.00E+13	0	100.42
110.	SBO+BR+M=BRSBO+M	2.00E+16	0	0.00
111.	SBBR+O+M=BRSBO+M	4.00E+16	0	0.00
112.	SBBR+SBO=BRSBO+SB	2.00E+12	0	27.20
113.	SBBR+SBO2=BRSBO+SBO	4.00E+12	0	18.83
114.	SBBR+SBO3=BRSBO+SBO2	1.00E+13	0	2.09
115.	SBO+BR2=BRSBO+BR	3.00E+13	0	20.92
116.	BROH+SBBR=HBR+BRSBO	1.50E+11	0	10.46
117.	BRSBO+BROH=BR2+HOSBO	7.00E+11	0	33.47
118.	SBO+CH3BR=BRSBO+CH3	5.00E+12	0	46.02
119.	CH3BR+SBO2=CH3O+BRSBO	4.00E+12	0	46.02

120. SBBR2+BR=SBBR3	2.00E+13	0	0.00
121. SBBR+BR=SBBR2	2.50E+13	0	0.00
122. SBBR3+H=SBBR2+HBR	1.02E+13	0	27.20
123. SBBR3+OH=SBBR2+BROH	4.00E+13	0	83.68
124. SBBR3+O=SBBR2+BRO	2.20E+13	0	75.31
125. SBBR3+CH3=SBBR2+CH3BR	2.00E+13	0	41.84
126. SBBR3+C2H5=C2H5BR+SBBR2	1.00E+13	0	41.84
127. SBBR3+SBO=BRSBO+SBBR2	8.00E+12	0	39.75
128. SBBR2+H=HBR+SBBR	1.50E+13	0	41.84
129. SBBR2+O=SBBR+BRO	2.00E+13	0	71.13
130. SBBR2+O=BRSBO+BR	3.50E+12	0	4.18
131. SBBR2+OH=SBBR+BROH	2.00E+13	0	77.40
132. SBBR2+OH=BRSBO+HBR	2.70E+12	0	8.37
133. SBBR2+BR2=SBBR3+BR	3.30E+12	0	35.56
134. SBBR2+BR=SBBR+BR2	1.50E+13	0	79.50
135. SBBR2+CH3O=BRSBO+CH3BR	4.50E+11	0	16.74
136. SBBR2+BRO=BRSBO+BR2	3.00E+11	0	6.28
137. SBBR+SBBR=SB+SBBR2	5.00E+12	0	33.47
138. SBBR2+SBBR2=SBBR+SBBR3	4.00E+12	0	46.02
139. SBBR2+SBO=SBBR+BRSBO	9.00E+12	0	39.75
140. SBBR2+SBO2=BRSBO+BRSBO	3.10E+12	0	8.37
141. SBBR+H=HBR+SB	2.00E+13	0	4.18
142. SBBR+O=SBO+BR	1.00E+13	0	4.18
143. SBBR+O=SB+BRO	2.00E+13	0	41.84
144. SBBR+OH=HBR+SBO	2.50E+12	0	20.92
145. SBBR+OH=BROH+SB	5.00E+12	0	37.66
146. SBBR+CH3=CH3BR+SB	8.00E+12	0	25.10
147. SBBR+CH3O=CH3+BRSBO	1.00E+13	0	27.20
148. SBBR+HOSBO2=BRSBO+HOSBO	2.50E+12	0	8.37
149. SBBR+BR=SB+BR2	2.00E+13	0	41.84
150. SBBR+BRO=BRSBO+BR	1.00E+13	0	0.00
151. SB+BR+M=SBBR+M	2.00E+15	0	0.00
152. BRO+SBO=BR+SBO2	1.00E+13	0	18.83
153. SBBR+O2=BR+SBO2	2.00E+12	0	41.84
154. BR+SBO3=BRO+SBO2	1.50E+13	0	33.47
155. SBO2+HBR=BR+HOSBO	2.00E+11	0	17.99
156. SBO3+HBR=BR+HOSBO2	2.00E+12	0	6.28
157. BRO+HOSBO=BR+HOSBO2	1.00E+12	0	41.84
158. HBR+SBO2=BRSBO+OH	1.50E+12	0	50.21
159. BR+SBO3=BRSBO+O2	2.30E+12	0	12.55
160. CH2+SBBR=CH2BR+SB	2.00E+13	0	14.64
161. CH2BR+SBO=CH2O+SBBR	2.00E+12	0	0.00
162. CH2+BRSBO=CH2BR+SBO	3.00E+13	0	43.93
163. CH2BR+SBO2=CH2O+BRSBO	6.00E+12	0	8.37

164. BRO+SB=SBO+BR	4.00E+13	0	16.74
165. HBR+SBO3=BRO+HOSBO	8.00E+11	0	12.55
166. BROH+SBO2=BRO+HOSBO	2.00E+13	0	37.66
167. BROH+SBO3=BRO+HOSBO2	1.50E+13	0	16.74
168. BROH+SB=HBR+SBO	7.50E+11	0	29.29
169. BROH+SBO=HBR+SBO2	5.00E+11	0	33.47
170. SBBR+SB=SB2+BR	2.00E+13	0	25.10
171. SBBR+SBBR=BR2+SB2	8.00E+11	0	32.64
172. BRO+SB2=SBO+SBBR	2.00E+12	0	41.84
173. SBH+SBBR=SB2+HBR	1.00E+12	0	10.46
174. SBH+BR=HBR+SB	1.50E+13	0	18.83
175. SBH+BR2=SBBR+HBR	2.00E+12	0	20.92
176. SBH+CH2BR=SB+CH3BR	9.00E+12	0	4.18
177. SBOH+SBBR=SB2+BROH	5.00E+11	0	37.66
178. SBOH+BR=SBO+HBR	1.00E+13	0	33.47
179. SBOH+CH2BR=SBO+CH3BR	4.00E+12	0	20.92

* Husain, D.; Slater, N.K.H., Kinetic study of ground state antimony atoms Sb($5^4S_{3/2}$) by atomic absorption spectroscopy, J.Photochem, 1977, 7,59-70.

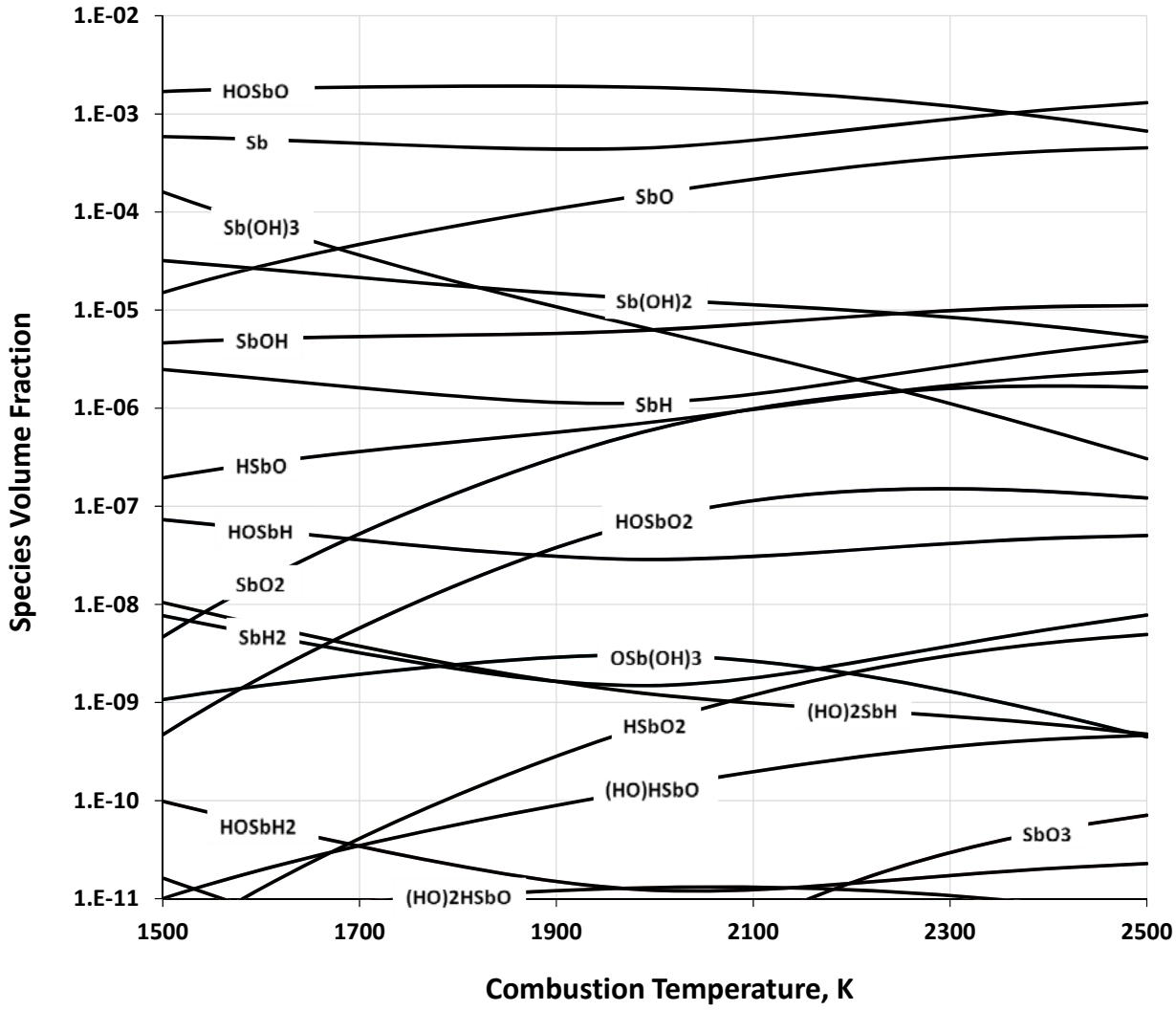

Figure 1 - Equilibrium concentrations vs. temperature of antimony-containing species in the combustion products of a stoichiometric methane/air flame, with an initial SbH_3 volume fraction of 0.25 %.

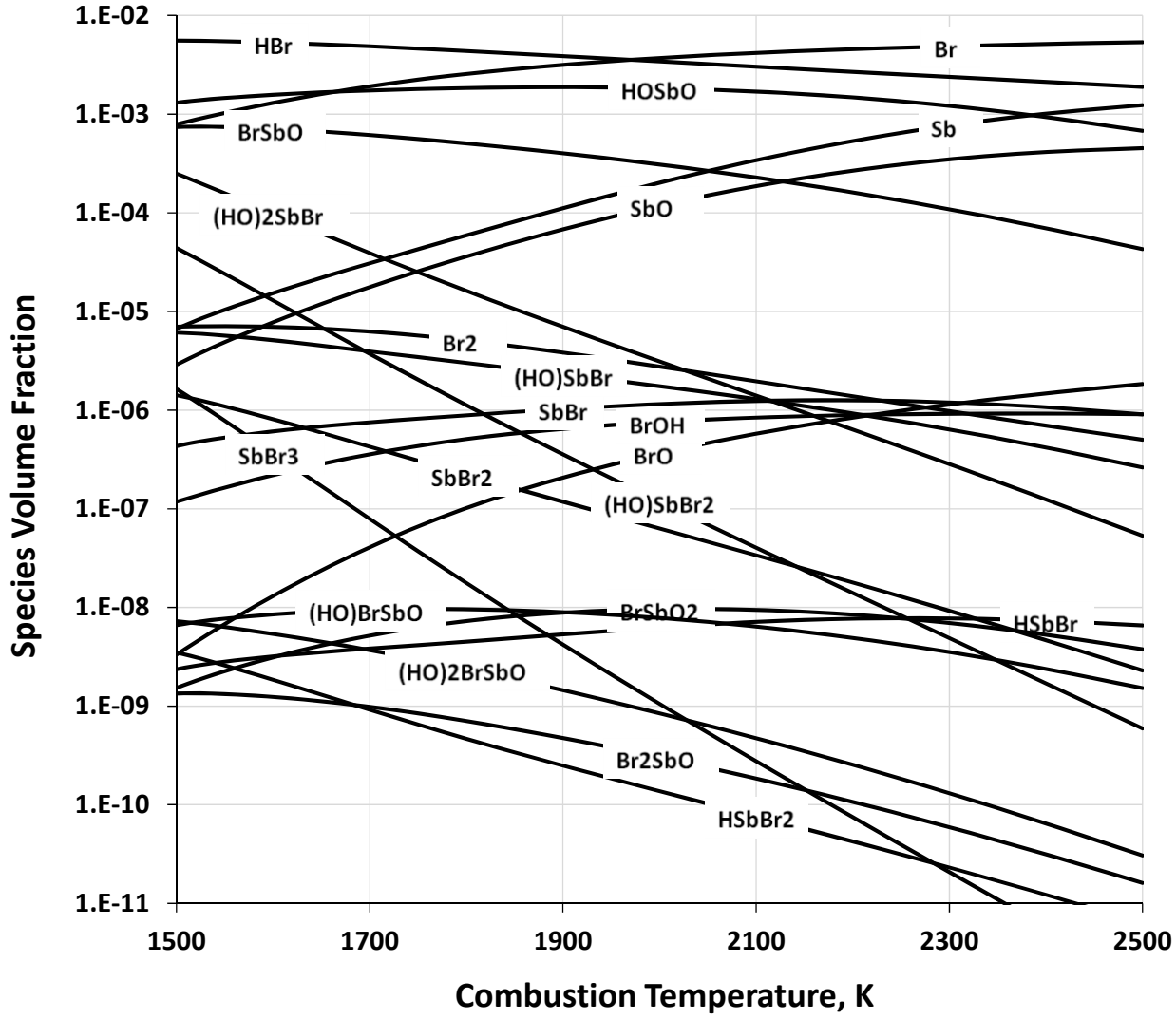

Figure 2 - Equilibrium concentrations of antimony compounds vs. equivalence ratio of methane/air flame with $SbBr_3$ added at a volume fraction of 0.25 %.

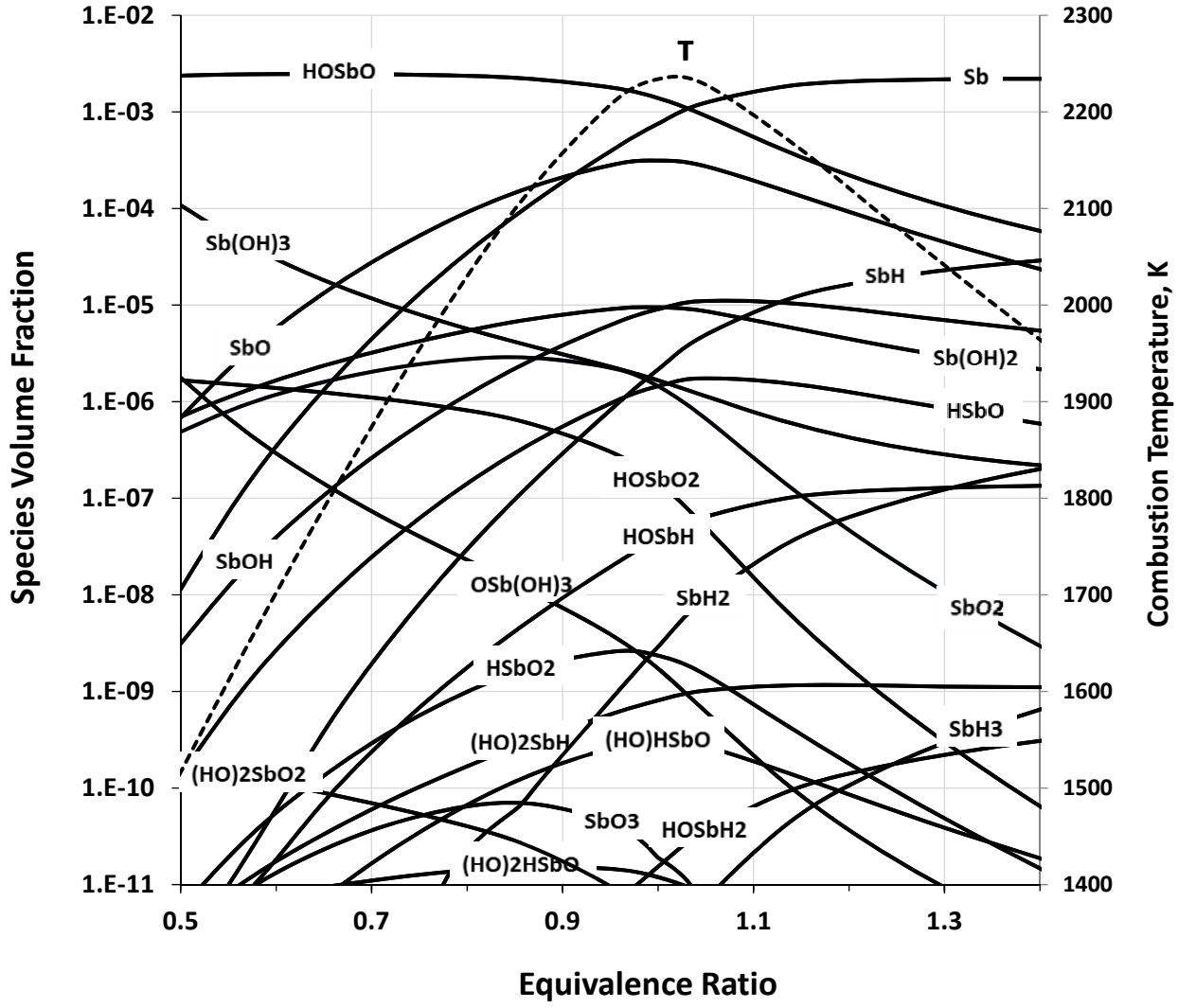

Figure 3 - Equilibrium concentrations of antimony-containing species vs. equivalence ratio of methane/air flame for an initial volume $SbBr_3$ volume fraction of 0.25 %.

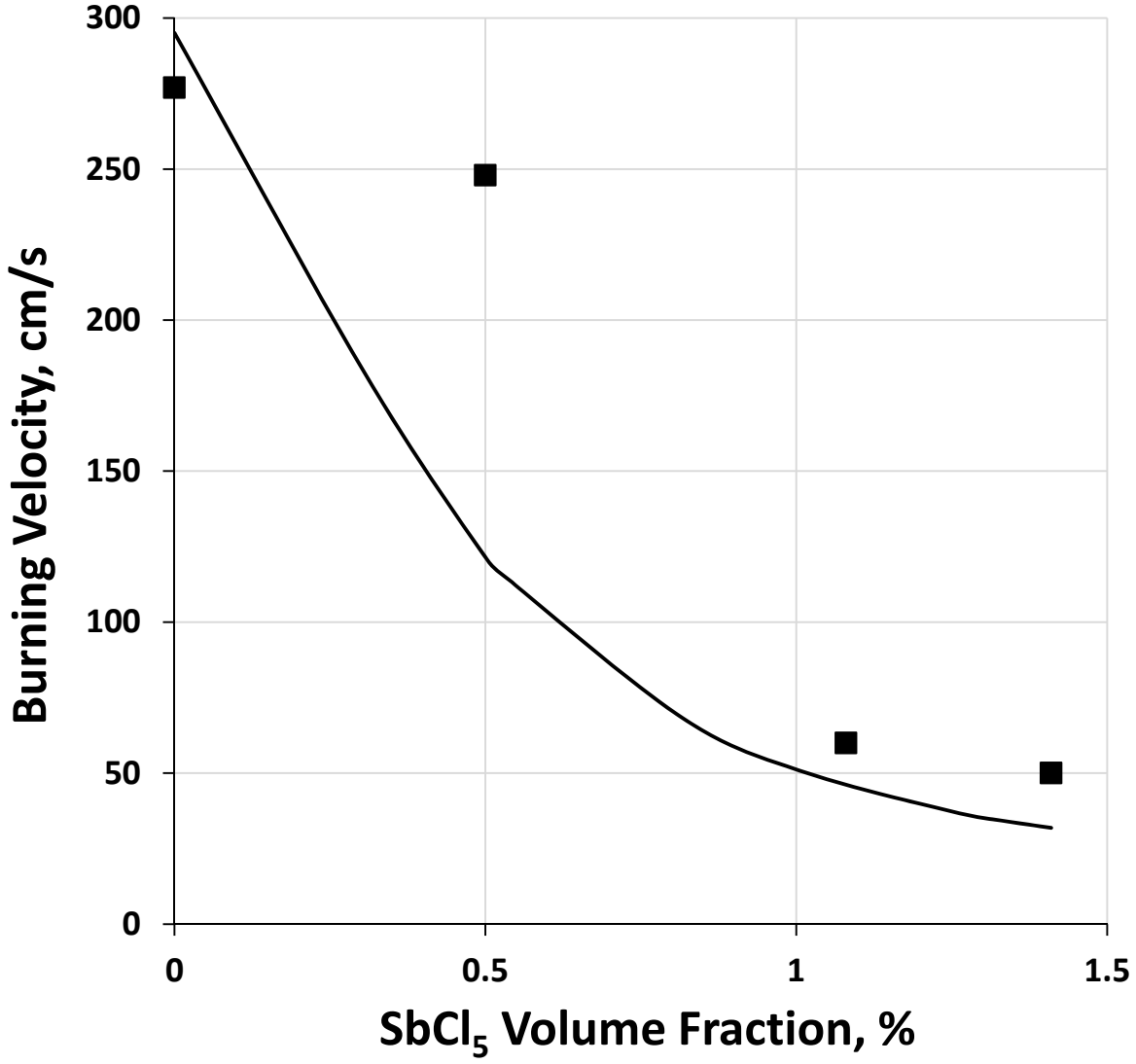

Figure 4 - Laminar burning velocity of hydrogen-air flames (298 K, 1 bar, equivalence ratio 1.75) with added $SbCl_5$ (■ – experiment; line: numerical prediction).

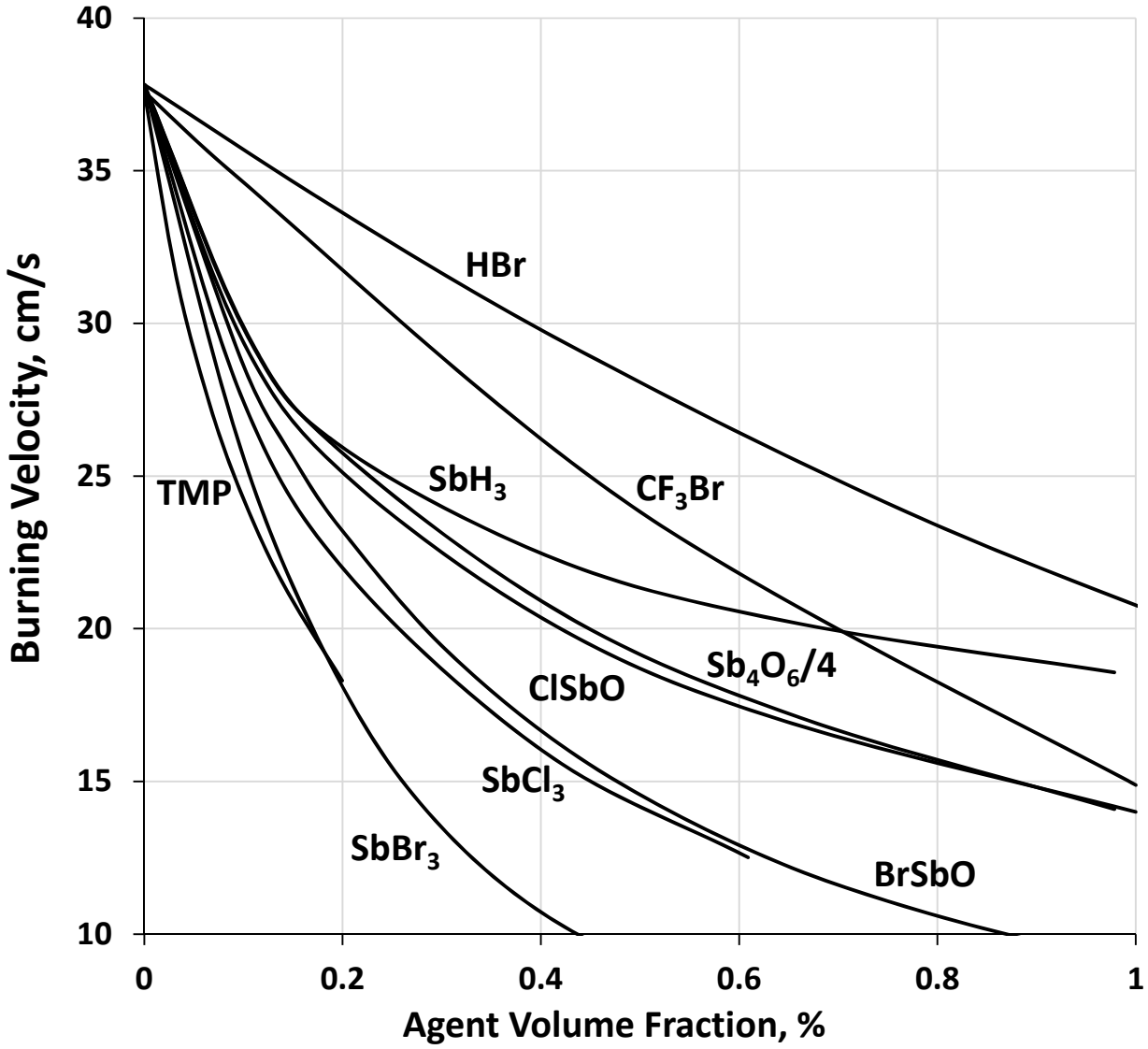

Figure 5 - Laminar burning velocity of stoichiometric methane-air flames (298 K, 1 bar) as a function of inhibitor volume fraction.

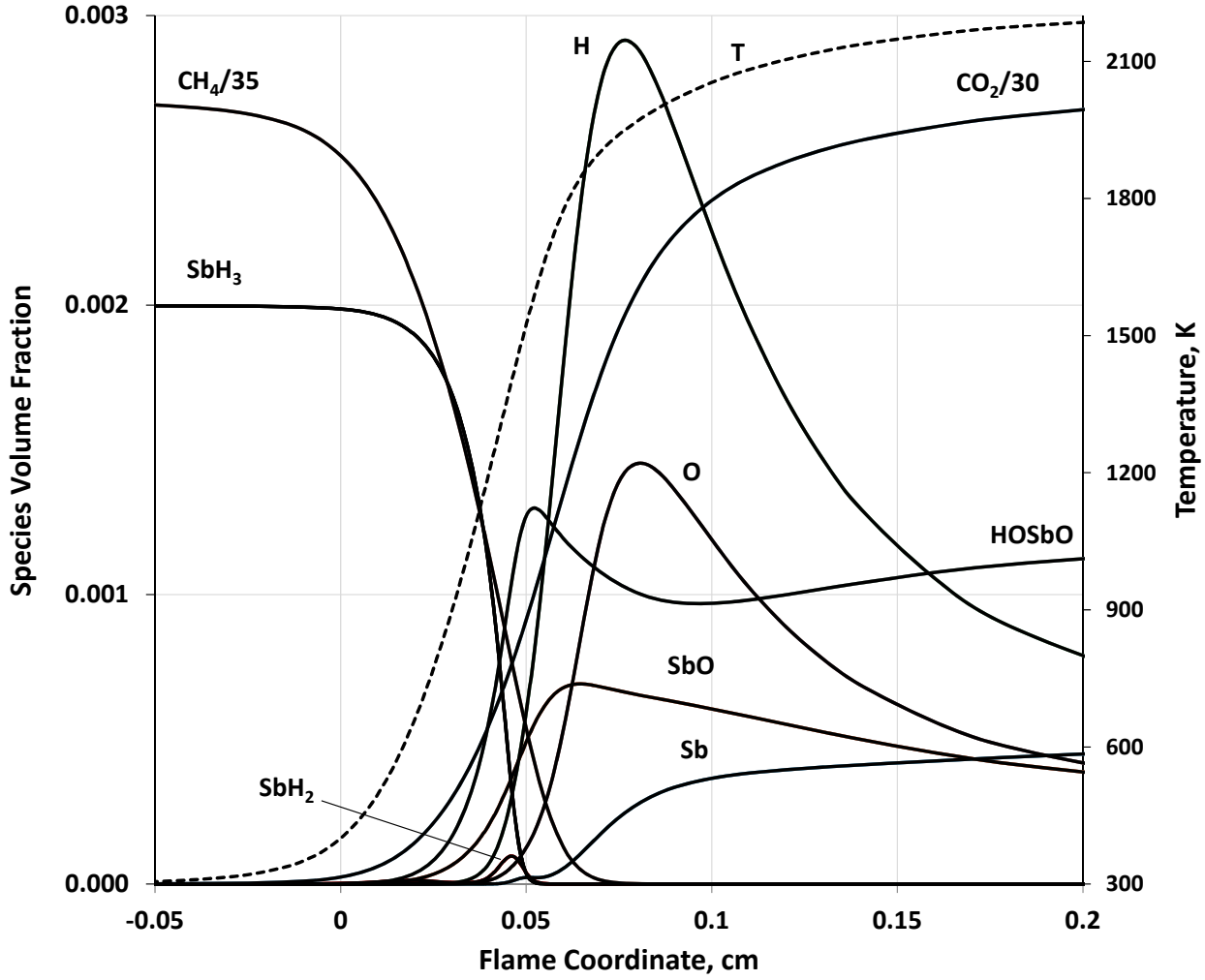

Figure 6 - Flame structure of stoichiometric methane/air flame inhibited by SbH_3 (298K, 1 bar, SbH_3 volume fraction of 0.2 %).

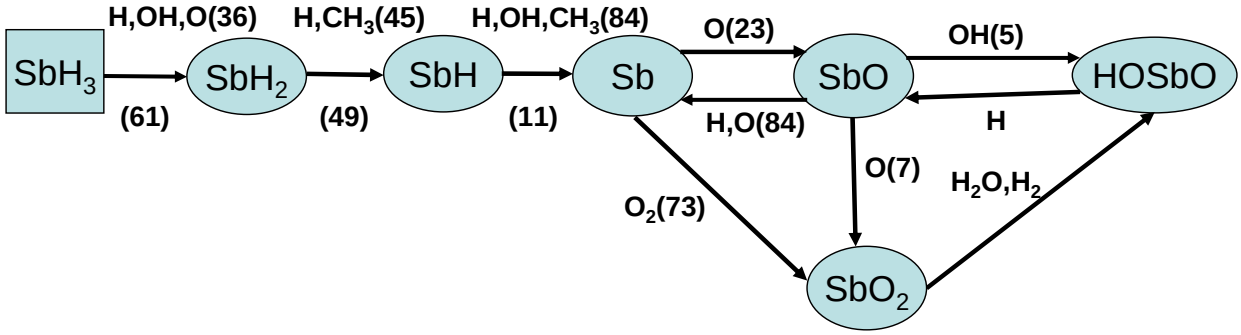

Figure 7 - The major reaction pathways of antimony-containing species in main reaction zone of a stoichiometric methane/air flame (with an initial SbH_3 volume fraction 0.25 %).

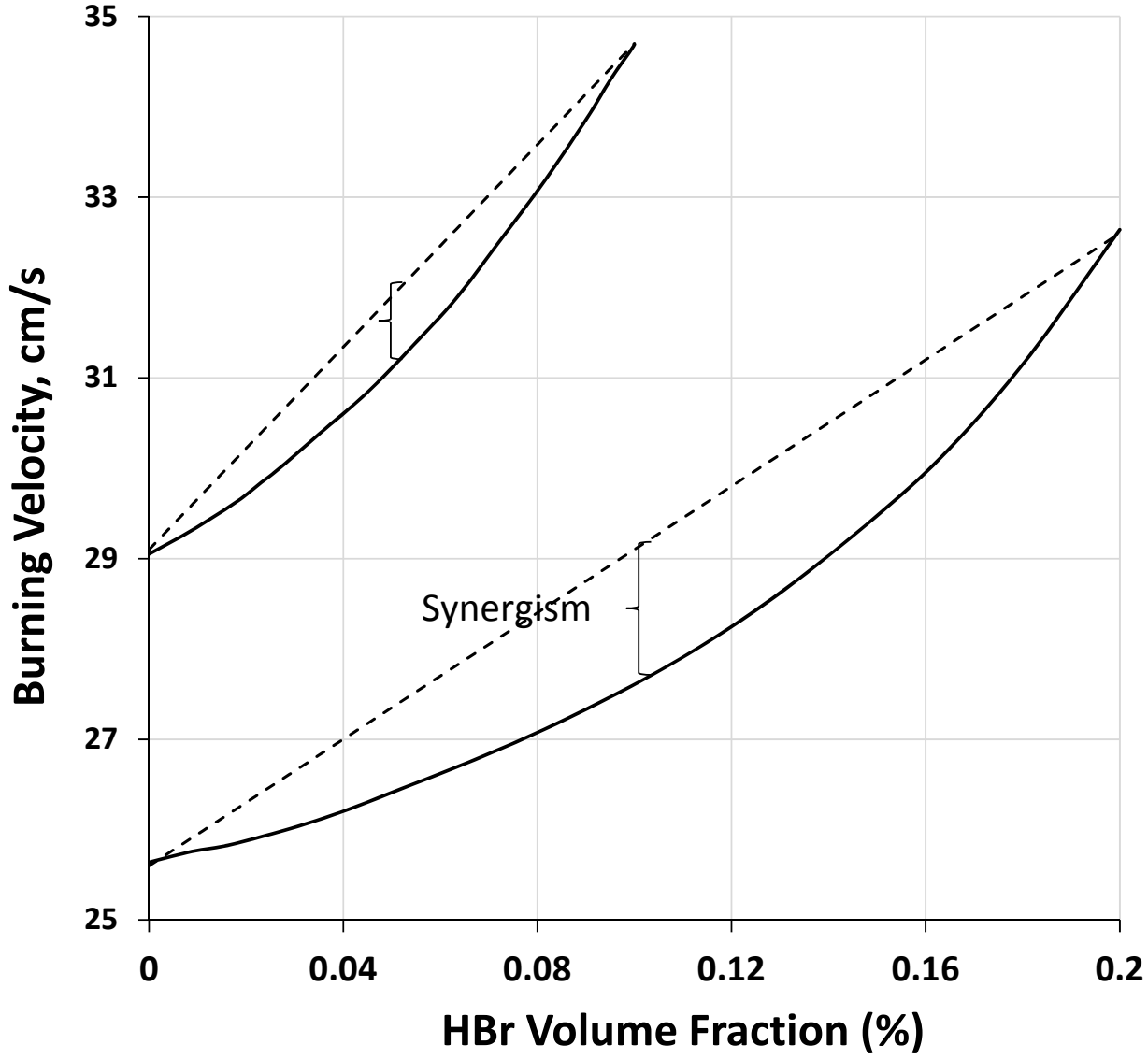

Figure 8 - Burning velocity vs. HBr volume fraction in the reactants (inhibitor is a mixture of SbH_3+HBr, added at either 0.001 or 0.002 volume fraction, to the stoichiometric methane/air flame (298 K, 1.01 bar).

Supplemental Material

1. Thermodynamic polynomials (Chemkin format) for antimony-containing species

```
SB        GAS     B04/09SB 1.   0.   0.   0.G   298.150  2000.000 1000.        1
 2.42087320E+00 3.48363006E-04-4.87492847E-07 2.56072866E-10-3.56862582E-14    2
 3.10833210E+04 7.80249403E+00 2.48973416E+00 7.79283907E-05-2.04107407E-07    3
 2.17573104E-10-7.89982814E-14 3.10735029E+04 7.47922252E+00 3.18178702E+04    4
SB(CH3)2          T04/09SB  1C   2H   6    0G   200.000  6000.000 1000.        1
 6.74202280E+00 1.59118082E-02-5.63150175E-06 8.99396716E-10-5.34173531E-14    2
 1.42205311E+04-4.60822517E+00 4.74741966E+00 1.27189509E-02 1.70266233E-05    3
-2.86489118E-08 1.20242266E-11 1.52304029E+04 7.86382523E+00 1.73106533E+04    4
SB(CH3) triplet 63005   H   3C   1SB  1    0G   300.000  3000.000 1000.00     1
 0.29697576E+01 0.11082103E-01-0.54282368E-05 0.12913154E-08-0.12107738E-12    2
 0.24777201E+05 0.12841121E+02 0.20779578E+01 0.14966753E-01-0.11965446E-04    3
 0.62789806E-08-0.15643845E-11 0.24947490E+05 0.17083682E+02                   4
SB(CH3)3          T04/09SB 1.C  3.H  9.   0.G   200.000  6000.000 1000.        1
 1.06182218E+01 2.18958190E-02-7.80204951E-06 1.25201509E-09-7.46171333E-14    2
-1.74686603E+02-2.48860995E+01 6.79004650E+00 1.80286318E-02 2.81660699E-05    3
-4.64556708E-08 1.93603118E-11 1.63764483E+03-1.51504424E+00 4.62959333E+03    4
SB(s) REF ELEM    B04/09SB 1.   0.   0.   0.S   298.150   904.000  904.        1
 0.00000000E+00 0.00000000E+00 0.00000000E+00 0.00000000E+00 0.00000000E+00    2
 0.00000000E+00 0.00000000E+00 2.12273784E+00 6.03818322E-03-1.41050855E-05    3
 1.52517658E-08-5.38507268E-12-8.04252525E+02-7.91696068E+00 0.00000000E+00    4
SB(l) REF ELEMENT B04/09SB 1.   0.   0.   0.L   904.000  1891.000 1000.        1
 3.74764275E+00 7.774849671-05-8.31208796E-08 3.86360546E-11-6.61471942E-15    2
 9.90188439E+02-1.38262406E+01 3.74764275E+00 7.77484967E-05-8.31208796E-08    3
 3.86360546E-11-6.61471942E-15 9.90188439E+02-1.38262406E+01 0.00000000E+00    4
SB2               T01/09SB 2.   0.   0.   0.G   200.000  6000.000 1000.        1
 4.44926335E+00 8.50731434E-05-2.15467387E-08 3.72963655E-12-2.34166278E-16    2
 2.70431984E+04 5.37301663E+00 3.59804769E+00 5.06905048E-03-1.10928478E-05    3
 1.08165334E-08-3.87449857E-12 2.71645110E+04 9.16897750E+00 2.83841140E+04    4
SBF               T03/09SB 1.F  1.   0.   0.G   200.000  6000.000 1000.        1
 5.03332293E+00-5.75565879E-04 3.29303124E-07-6.53261567E-11 4.37256522E-15    2
-1.04517631E+04-2.20146752E-01 1.97345005E+00 1.34491064E-02-2.34261965E-05    3
 1.76006797E-08-4.87093301E-12-9.92716684E+03 1.40999416E+01-8.91549833E+03    4
SBF3              T03/09SB 1.F  3.   0.   0.G   298.150  4000.000 1000.        1
 8.87021479E+00 1.35894382E-03-4.85074797E-07 7.63330680E-11-4.47034933E-15    2
-1.00544258E+05-1.47836086E+01 1.99190356E+00 3.69570851E-02-7.05841557E-05    3
 6.15822022E-08-2.01310886E-11-9.94498006E+04 1.67111795E+01-9.77247006E+04    4
SBH3              T01/09H  3.SB 1.   0.   0.G   200.000  6000.000 1000.        1
 5.19970155E+00 4.67661185E-03-1.77733186E-06 2.97629920E-10-1.82688048E-14    2
 1.52898503E+04-3.79348197E+00 3.19635148E+00 3.49548430E-03 1.29554549E-05    3
-1.84844825E-08 7.21553443E-12 1.62216027E+04 8.31215758E+00 1.74112966E+04    4
HOSBH              63005H   2O   1SB  1    0G   300.000  3000.000 1000.00     1
 0.55062345E+01 0.38618323E-02-0.16928074E-05 0.36746218E-09-0.31952322E-13    2
-0.36915097E+04 0.12740457E+01 0.36129284E+01 0.12138008E-01-0.15675216E-04    3
 0.11076976E-07-0.31419273E-11-0.33308721E+04 0.10275225E+02                   4
HOSBH2             63005H   3O   1SB  1    0G   300.000  3000.000 1000.00     1
 0.65664142E+01 0.64704513E-02-0.31693328E-05 0.75840330E-09-0.71668567E-13    2
-0.11467059E+05-0.64947408E+01 0.11231640E+01 0.30350268E-01-0.44093326E-04    3
 0.32739939E-07-0.95657784E-11-0.10418949E+05 0.19401095E+02                   4
(HO)2SBH           63005H   3O   2SB  1    0G   300.000  3000.000 1000.00     1
 0.95510723E+01 0.44967873E-02-0.16228254E-05 0.27821056E-09-0.18096696E-13    2
-0.44000076E+05-0.18436842E+02 0.13631867E+01 0.41254930E-01-0.64502959E-04    3
 0.48515593E-07-0.13945602E-10-0.42505062E+05 0.20207742E+02                   4
OSBH2              63005H   2O   1SB  1    0G   300.000  3000.000 1000.00     1
 0.51767448E+01 0.64813205E-02-0.36790232E-05 0.97868610E-09-0.99971483E-13    2
 0.20394495E+05 0.11577140E+01 0.20823002E+01 0.18583046E-01-0.23062058E-04    3
 0.15817357E-07-0.45628885E-11 0.21082004E+05 0.16292677E+02                   4
SBH triplet        63005H   1SB  1         0G   300.000  3000.000 1000.00     1
 0.28223176E+01 0.22108686E-02-0.12400284E-05 0.32752955E-09-0.33320693E-13    2
 0.28713354E+05 0.93069145E+01 0.38300626E+01-0.29123164E-02 0.81021818E-05    3
-0.70183160E-08 0.20857546E-11 0.28565778E+05 0.47165849E+01                   4
SBH2               63005H   2SB  1         0G   300.000  3000.000 1000.00     1
 0.30219090E+01 0.53025317E-02-0.29993734E-05 0.79719875E-09-0.81481891E-13    2
 0.23800088E+05 0.94325621E+01 0.38251193E+01-0.36711061E-04 0.79289000E-05    3
-0.82544608E-08 0.25779368E-11 0.23754773E+05 0.61116533E+01                   4
SB4O6                0SB  4O   6          G   300.000  3000.000 1000.00     1
 0.24589789E+02 0.47494815E-02-0.25327138E-05 0.57598828E-09-0.44940939E-13    2
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-0.15492415E+06-0.86828366E+02 0.10674493E+02 0.63281847E-01-0.94638035E-04    3
 0.64850717E-07-0.16831419E-10-0.15228465E+06-0.20412902E+02                   4
SB2O3(s1)              0SB  2O   3          S   300.000   879.000  879.00     1
 0.51026398E+01 0.44858656E-01-0.89633694E-04 0.88201979E-07-0.31403328E-10    2
-0.88102849E+05-0.23556201E+02 0.51026398E+01 0.44858656E-01-0.89633694E-04    3
 0.88201979E-07-0.31403328E-10-0.88102849E+05-0.23556201E+02                   4
SB2O3(s2)              0SB  2O   3          S   879.000   928.000  928.00     1
 0.37193767E+02-0.50052660E-01 0.13804977E-05 0.65292323E-07-0.35657030E-10    2
-0.92917270E+05-0.18503585E+03 0.37193767E+02-0.50052660E-01 0.13804978E-05    3
 0.65292323E-07-0.35657030E-10-0.92917270E+05-0.18503585E+03                   4
SB2O3(l)               0SB  2O   3          L   928.000  3000.000 1500.00    1
 0.21649435E+02 0.00000000E+00 0.00000000E+00 0.00000000E+00 0.00000000E+00    2
-0.79489385E+05-0.10689445E+03 0.21649435E+02 0.00000000E+00 0.00000000E+00    3
 0.00000000E+00 0.00000000E+00-0.79489385E+05-0.10689445E+03                   4
HOSBO                  0H   1O   2SB  1     G   300.000  3000.000 1000.00    1
 0.66922159E+01 0.35199344E-02-0.17559185E-05 0.44019652E-09-0.44161519E-13    2
-0.30306806E+05-0.29610411E+01 0.23644721E+01 0.22996511E-01-0.34219184E-04    3
 0.24247975E-07-0.65375063E-11-0.29549537E+05 0.17376421E+02                   4
HOSBO2                 0H   1O   3SB  1     G   300.000  3000.000 1000.00    1
 0.89896566E+01 0.46249570E-02-0.24616815E-05 0.64573428E-09-0.66696994E-13    2
-0.33392996E+05-0.12331544E+02 0.35728917E+01 0.28234917E-01-0.40790970E-04    3
 0.28141493E-07-0.74263616E-11-0.32406788E+05 0.13315490E+02                   4
OSB(OH)3               0H   3O   4SB  1     G   300.000  3000.000 1000.00    1
 0.13546942E+02 0.80029250E-02-0.35310995E-05 0.79287198E-09-0.72781706E-13    2
-0.90893276E+05-0.33443549E+02 0.46238869E+01 0.48559205E-01-0.71661608E-04    3
 0.51077270E-07-0.13859896E-10-0.89351868E+05 0.83890209E+01                   4
BR3SBO                 0BR  3O   1SB  1     G   300.000  3000.000 1000.00    1
 0.90206346E+01 0.16376841E-02-0.10965824E-05 0.33124247E-09-0.37371571E-13    2
-0.23946925E+05-0.12139325E+01 0.66573533E+01 0.11923680E-01-0.17774882E-04    3
 0.12282980E-07-0.32335235E-11-0.23515912E+05 0.99793163E+01                   4
BR2SBO                 0BR  2O   1SB  1     G   300.000  3000.000 1000.00    1
 0.83257254E+01 0.11594496E-02-0.79165486E-06 0.24253146E-09-0.27652401E-13    2
-0.78501404E+04-0.18076398E+01 0.64342268E+01 0.96725199E-02-0.14981874E-04    3
 0.10649754E-07-0.28662269E-11-0.75191945E+04 0.70809786E+01                   4
BRSBO                  0BR  1O   1SB  1     G   300.000  3000.000 1000.00    1
 0.62486065E+01 0.12250784E-02-0.80493231E-06 0.23967973E-09-0.26743161E-13    2
-0.85508315E+04 0.27436023E+01 0.46546525E+01 0.78463013E-02-0.11104877E-04    3
 0.73517166E-08-0.18661041E-11-0.82443110E+04 0.10372157E+02                   4
BRSBO2                 0BR  1O   2SB  1     G   300.000  3000.000 1000.00    1
 0.85646991E+01 0.23364779E-02-0.15332999E-05 0.45612541E-09-0.50855512E-13    2
-0.11543010E+05-0.74939329E+01 0.55403556E+01 0.14853830E-01-0.20939294E-04    3
 0.13813432E-07-0.34951767E-11-0.10959140E+05 0.69917820E+01                   4
H2SBBR                 0H   2BR  1SB  1     G   300.000  3000.000 1000.00    1
 0.44069287E+01 0.63327430E-02-0.36983810E-05 0.10111142E-08-0.10586277E-12    2
 0.56346552E+04 0.86270818E+01 0.40442866E+01 0.64699184E-02-0.19340543E-05    3
-0.14784967E-08 0.84488824E-12 0.57728533E+04 0.10704969E+02                   4
(HO)2BRSBO             0H   2O   3BR  1SB  1G   300.000  3000.000 1000.00    1
 0.13127475E+02 0.57253570E-02-0.26121776E-05 0.60586247E-09-0.57181406E-13    2
-0.68791291E+05-0.27728281E+02 0.66508506E+01 0.34995517E-01-0.51562913E-04    3
 0.36603350E-07-0.98974692E-11-0.67664149E+05 0.26767704E+01                   4
(HO)2HSBO              0H   3O   3SB  1     G   300.000  3000.000 1000.00    1
 0.99972191E+01 0.85726928E-02-0.42416349E-05 0.10452962E-08-0.10275489E-12    2
-0.58616622E+05-0.17780762E+02 0.36408416E+01 0.36990594E-01-0.51357075E-04    3
 0.35447981E-07-0.94515240E-11-0.57494966E+05 0.12136987E+02                   4
(HO)2SBBR              0H   2O   2SB  1BR  1G   300.000  3000.000 1000.00    1
 0.10901942E+02 0.45418556E-02-0.18773908E-05 0.39711746E-09-0.34770543E-13    2
-0.63001920E+05-0.18788810E+02 0.52333168E+01 0.31304336E-01-0.48153080E-04    3
 0.35335557E-07-0.97913752E-11-0.62072594E+05 0.75370349E+01                   4
(HO)2BRSBO             0H   2O   3SB  1BR  1G   300.000  3000.000 1000.00    1
 0.13127475E+02 0.57253570E-02-0.26121776E-05 0.60586247E-09-0.57181406E-13    2
-0.68791291E+05-0.27728281E+02 0.66508506E+01 0.34995517E-01-0.51562913E-04    3
 0.36603350E-07-0.98974692E-11-0.67664149E+05 0.26767704E+01                   4
(HO)2SBO2              0H   2O   4SB  1     G   300.000  3000.000 1000.00    1
 0.11908105E+02 0.61269867E-02-0.28970441E-05 0.69536309E-09-0.67568449E-13    2
-0.54266126E+05-0.23191822E+02 0.45838985E+01 0.39342664E-01-0.58598839E-04    3
 0.41748745E-07-0.11310627E-10-0.52997227E+05 0.11163527E+02                   4
(HO)3SBO               0H   3O   4SB  1     G   300.000  3000.000 1000.00    1
 0.13546942E+02 0.80029250E-02-0.35310995E-05 0.79287198E-09-0.72781706E-13    2
-0.90893276E+05-0.33443549E+02 0.46238869E+01 0.48559205E-01-0.71661608E-04    3
 0.51077270E-07-0.13859896E-10-0.89351868E+05 0.83890209E+01                   4
(HO)BRSBO              0H   1O   2SB  1BR  1G   300.000  3000.000 1000.00    1
 0.99731874E+01 0.30890986E-02-0.14902479E-05 0.36545427E-09-0.36217958E-13    2
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-0.28780873E+05-0.13333367E+02 0.59809620E+01 0.21590724E-01-0.33041773E-04    3
 0.23932529E-07-0.65611676E-11-0.28109064E+05 0.52936322E+01                   4
(HO)HSBO               0H   2O   2SB  1     G   300.000  3000.000 1000.00     1
 0.77520919E+01 0.61897322E-02-0.33238851E-05 0.87220667E-09-0.89747306E-13    2
-0.16150882E+05-0.84591473E+01 0.32354385E+01 0.26050079E-01-0.35805004E-04    3
 0.24320019E-07-0.64001336E-11-0.15337238E+05 0.12882661E+02                   4
(HO)(CH3)SBBR          0H   4O   1SB  1C   1G   300.000  3000.000 1000.00BR   1
 0.71245581E+01 0.11976996E-01-0.59571046E-05 0.14537541E-08-0.14040846E-12    2
-0.34562616E+05 0.13928258E+01 0.19959884E+01 0.33358104E-01-0.39329010E-04    3
 0.24568520E-07-0.61358073E-11-0.33580244E+05 0.25918503E+02                   4
(HO)SBBR               0H   1O   1SB  1BR  1G   300.000  3000.000 1000.00     1
 0.75366101E+01 0.21259897E-02-0.84469577E-06 0.17121481E-09-0.14404435E-13    2
-0.17922386E+05-0.34398613E+01 0.48081678E+01 0.15086137E-01-0.23354483E-04    3
 0.17224118E-07-0.47892246E-11-0.17479016E+05 0.92117009E+01                   4
(HO)SBBR2              0H   1O   1SB  1BR  2G   300.000  3000.000 1000.00     1
 0.93562426E+01 0.24473046E-02-0.10677992E-05 0.24024225E-09-0.22326988E-13    2
-0.41432760E+05-0.75255722E+01 0.61043931E+01 0.17859786E-01-0.27794146E-04    3
 0.20462890E-07-0.56792598E-11-0.40902644E+05 0.75614514E+01                   4
(HO)SBO                0H   1O   2SB  1     G   300.000  3000.000 1000.00     1
 0.66922159E+01 0.35199344E-02-0.17559185E-05 0.44019652E-09-0.44161519E-13    2
-0.30306806E+05-0.29610411E+01 0.23644721E+01 0.22996511E-01-0.34219184E-04    3
 0.24247975E-07-0.65375063E-11-0.29549537E+05 0.17376421E+02                   4
(HO)SBO2               0H   1O   3SB  1     G   300.000  3000.000 1000.00     1
 0.89896566E+01 0.46249570E-02-0.24616815E-05 0.64573428E-09-0.66696994E-13    2
-0.33392996E+05-0.12331544E+02 0.35728917E+01 0.28234917E-01-0.40790970E-04    3
 0.28141493E-07-0.74263616E-11-0.32406788E+05 0.13315490E+02                   4
HSBBR                  0H   1BR  1SB  1     G   300.000  3000.000 1000.00     1
 0.47905847E+01 0.30746979E-02-0.18120556E-05 0.49951176E-09-0.52678010E-13    2
 0.14283639E+05 0.69967429E+01 0.44532155E+01 0.41653477E-02-0.30597896E-05    3
 0.10725073E-08-0.13122013E-12 0.14364054E+05 0.86890612E+01                   4
HSBBR2                 0H   1BR  2SB  1     G   300.000  3000.000 1000.00     1
 0.63114149E+01 0.38987785E-02-0.23747212E-05 0.67187981E-09-0.72329256E-13    2
-0.63087434E+04 0.48784322E+01 0.46190271E+01 0.11079863E-01-0.13763649E-04    3
 0.86760318E-08-0.21762506E-11-0.59908425E+04 0.12940342E+02                   4
HSBO                   0H   1O   1SB  1     G   300.000  3000.000 1000.00     1
 0.43249036E+01 0.38855506E-02-0.23541319E-05 0.66084305E-09-0.70549134E-13    2
 0.92983775E+04 0.63149527E+01 0.28671228E+01 0.86390978E-02-0.78680889E-05    3
 0.32592385E-08-0.45075403E-12 0.96438124E+04 0.13617296E+02                   4
HSBO2                  0H   1O   2SB  1     G   300.000  3000.000 1000.00     1
 0.64474457E+01 0.52659794E-02-0.32463687E-05 0.92452434E-09-0.99874002E-13    2
 0.19208840E+02-0.21247668E+01 0.33513262E+01 0.17255357E-01-0.20637786E-04    3
 0.12123702E-07-0.28008935E-11 0.65818773E+03 0.12910995E+02                   4
(CH3)2SBBR             0H   6BR  1SB  1C   2G   300.000  3000.000 1000.00     1
 0.33390036E+01 0.19747229E-01-0.93226638E-05 0.21504051E-08-0.19653412E-12    2
-0.76162709E+04 0.22132582E+02 0.56300836E+00 0.33135291E-01-0.32830880E-04    3
 0.20106631E-07-0.52566109E-11-0.71752760E+04 0.34954134E+02                   4
(CH3O)SBO              0H   3O   2SB  1C   1G   300.000  3000.000 1000.00     1
 0.51744657E+01 0.13589945E-01-0.69103373E-05 0.16996246E-08-0.16398752E-12    2
-0.26441909E+05 0.77395613E+01 0.38035445E+01 0.17199160E-01-0.95124539E-05    3
 0.15598989E-08 0.33956143E-12-0.26074002E+05 0.14822081E+02                   4
(CH3O)SBO2             0H   3O   3SB  1C   1G   300.000  3000.000 1000.00     1
 0.75978840E+01 0.14455777E-01-0.74613300E-05 0.18617147E-08-0.18200026E-12    2
-0.29405786E+05-0.58102384E+01 0.48058834E+01 0.23932985E-01-0.19140949E-04    3
 0.79573327E-08-0.12832061E-11-0.28762846E+05 0.80822497E+01                   4
CH3SBBR                0H   3C   1SB  1BR  1G   300.000  3000.000 1000.00     1
 0.47737947E+01 0.81694213E-02-0.41195057E-05 0.10108226E-08-0.97681915E-13    2
 0.80613140E+04 0.11623783E+02 0.28138346E+01 0.16639769E-01-0.17770789E-04    3
 0.10742185E-07-0.26881495E-11 0.84217806E+04 0.20921831E+02                   4
CH3SBBR2               0H   3C   1SB  1BR  2G   300.000  3000.000 1000.00     1
 0.71486110E+01 0.89501987E-02-0.50599469E-05 0.13555426E-08-0.14005275E-12    2
-0.14734692E+05 0.39044471E+01 0.38553074E+01 0.19961747E-01-0.18334771E-04    3
 0.80437593E-08-0.12716904E-11-0.13967948E+05 0.20333150E+02                   4
CH3SBO2                0H   3O   2SB  1C   1G   300.000  3000.000 1000.00     1
 0.75580475E+01 0.99368574E-02-0.52204933E-05 0.13299830E-08-0.13277433E-12    2
-0.90381881E+04-0.25478572E+01 0.28850746E+01 0.29108072E-01-0.34696298E-04    3
 0.21459842E-07-0.52850698E-11-0.81275597E+04 0.19876705E+02                   4
SBBR                   0BR  1SB  1           G   300.000  3000.000 1000.00     1
 0.44043655E+01 0.17355236E-03-0.12287420E-06 0.38616878E-10-0.44858548E-14    2
 0.21019163E+05 0.71538896E+01 0.40770664E+01 0.17341508E-02-0.28408752E-05    3
 0.21020198E-08-0.58318713E-12 0.21072053E+05 0.86700678E+01                   4
SBBR2                  0BR  2SB  1           G   300.000  3000.000 1000.00     1
 0.58172539E+01 0.33188141E-03-0.23508292E-06 0.73906183E-10-0.85872063E-14    2
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 0.18174069E+04 0.78061678E+01 0.51904986E+01 0.33225329E-02-0.54465052E-05    3
 0.40318178E-08-0.11189726E-11 0.19185764E+04 0.10708993E+02                   4
SBBR3                   0BR  3SB  1          G   300.000  3000.000 1000.00     1
 0.77163181E+01 0.51563412E-03-0.36544698E-06 0.11493506E-09-0.13358105E-13    2
-0.19141187E+05 0.31637587E+01 0.67410205E+01 0.51734925E-02-0.84872364E-05    3
 0.62861292E-08-0.17453236E-11-0.18983961E+05 0.76798390E+01                   4
SBO                     0O   1SB  1          G   300.000  3000.000 1000.00     1
 0.38993692E+01 0.96143474E-03-0.62265889E-06 0.18331443E-09-0.20270745E-13    2
 0.15315593E+05 0.68091294E+01 0.27398060E+01 0.55649946E-02-0.74759595E-05    3
 0.47174887E-08-0.11451411E-11 0.15549240E+05 0.12412024E+02                   4
SBO2                    0O   2SB  1          G   300.000  3000.000 1000.00     1
 0.44373834E+01 0.11426936E-03-0.81196127E-07 0.25581985E-10-0.29770086E-14    2
 0.21924466E+04 0.99553144E+01 0.42196614E+01 0.11582053E-02-0.19066715E-05    3
 0.14156133E-08-0.39374678E-12 0.22273386E+04 0.10962435E+02                   4
SBO3                    0O   3SB  1          G   300.000  3000.000 1000.00     1
 0.80354039E+01 0.16259181E-02-0.10943742E-05 0.33175783E-09-0.37525788E-13    2
 0.93571376E+04-0.59190868E+01 0.55363783E+01 0.12553130E-01-0.18881858E-04    3
 0.13121190E-07-0.34676613E-11 0.98103872E+04 0.59044897E+01                   4
SBOH                    0H   1O   1SB  1     G   300.000  3000.000 1000.00     1
 0.47522135E+01 0.17412028E-02-0.57729000E-06 0.88436902E-10-0.49001931E-14    2
 0.37155454E+04 0.41506999E+01 0.26484993E+01 0.11765773E-01-0.18028715E-04    3
 0.13332434E-07-0.37183277E-11 0.40558026E+04 0.13897476E+02                   4
SB(OH)2                 0H   2O   2SB  1     G   300.000  3000.000 1000.00     1
 0.82615074E+01 0.39224265E-02-0.14583960E-05 0.27002656E-09-0.20402408E-13    2
-0.36810705E+05-0.93188910E+01 0.34335647E+01 0.26896231E-01-0.41412152E-04    3
 0.30567897E-07-0.85103784E-11-0.36028218E+05 0.13057633E+02                   4
SB(OH)3                 0H   3O   3SB  1     G   300.000  3000.000 1000.00     1
 0.11464167E+02 0.66354891E-02-0.26944180E-05 0.55756429E-09-0.47711331E-13    2
-0.83821828E+05-0.25800188E+02 0.33318789E+01 0.45107417E-01-0.69316474E-04    3
 0.50915044E-07-0.14122775E-10-0.82492509E+05 0.11947706E+02                   4
CLSBO                   0CL  1O   1SB  1     G   300.000  3000.000 1000.00     1
 0.62486065E+01 0.12250784E-02-0.80493231E-06 0.23967973E-09-0.26743161E-13    2
-0.14790877E+05-0.24159838E-01 0.46546525E+01 0.78463013E-02-0.11104877E-04    3
 0.73517166E-08-0.18661041E-11-0.14484357E+05 0.76043950E+01                   4
SBCL2                T02/09SB 1.CL 2.   0.   0.G   200.000  6000.000 1000.       1
 5.93482013E+00 1.08999381E-03-4.26609277E-07 7.27977714E-11-4.52597505E-15    2
-1.38933126E+04-8.23285793E-01 3.26046441E+00 8.13468529E-03-5.31503869E-06    3
-1.00841552E-09 1.59478097E-12-1.31613843E+04 1.30106100E+01-1.18759133E+04    4
SBCL3                T02/09SB 1.CL 3.   0.   0.G   200.000  6000.000 1000.       1
 9.72981943E+00 2.86438114E-04-1.14493259E-07 1.98078808E-11-1.24319722E-15    2
-4.06639954E+04-1.46490216E+01 5.51759463E+00 2.44777531E-02-5.31507818E-05    3
 5.13625769E-08-1.82868138E-11-4.00472434E+04 4.23196216E+00-3.76909283E+04    4
SBCL5                T03/09SB 1.CL 5.   0.   0.G   200.000  6000.000 1000.       1
 1.54869771E+01 5.43850014E-04-2.17373802E-07 3.76055163E-11-2.36017400E-15    2
-5.68371308E+04-3.79009433E+01 7.49842062E+00 4.64325927E-02-1.00842443E-04    3
 9.74659896E-08-3.47058612E-11-5.56676517E+04-2.09441114E+00-5.20829249E+04    4
SBCL triplet 63005      CL  1SB  1    0    0G   300.000  3000.000 1000.00     1
 0.44258150E+01 0.98458925E-04-0.52892768E-07 0.13053074E-10-0.12234332E-14    2
 0.10023765E+05 0.56614704E+01 0.37460264E+01 0.32781339E-02-0.57973080E-05    3
 0.46820131E-08-0.14256546E-11 0.10146168E+05 0.88496041E+01                   4
SBCL4                   0CL  4SB  1          G   300.000  3000.000 1000.00     1
 0.90206346E+01 0.16376841E-02-0.10965824E-05 0.33124247E-09-0.37371571E-13    2
-0.37785735E+05-0.29400096E+01 0.66573533E+01 0.11923680E-01-0.17774882E-04    3
 0.12282980E-07-0.32335235E-11-0.37354723E+05 0.82532392E+01                   4
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2. Kinetic sub-model for SbCl5 and SbCl3

1.	SBCL5=SBCL4+CL	5.50E+15	0.0	67000.0
2.	SBCL4=SBCL3+CL	2.00E+15	0.0	30000.0
3.	SBCL3=SBCL2+CL	2.00E+16	0.0	85000.0
4.	SBCL2=SBCL+CL	2.00E+15	0.0	79000.0
5.	SBCL=SB+CL	3.00E+15	0.0	75000.0
6.	SBCL5+H=SBCL4+HCL	2.00E+13	0.0	2000.0
7.	SBCL5+OH=SBCL4+HOCL	2.30E+13	0.0	17000.0
8.	SBCL5+O=SBCL4+CLO	1.80E+13	0.0	11000.0
9.	SBCL5+CL=SBCL4+CL2	4.00E+12	0.0	15000.0
10.	SBCL4+H=SBCL3+HCL	1.00E+13	0.0	0.0
11.	SBCL4+OH=SBCL3+HOCL	5.00E+13	0.0	4000.0
12.	SBCL4+O=SBCL3+CLO	2.20E+13	0.0	1500.0

13.	SBCL3+H=SBCL2+HCL	2.00E+13	0.0	5500.0
14.	SBCL3+O=SBCL2+CLO	2.20E+13	0.0	19000.0
15.	SBCL3+CL=SBCL2+CL2	1.00E+13	0.0	27000.0
16.	SBCL3+CH3=SBCL2+CH3CL	8.00E+12	0.0	9500.0
17.	SBCL2+H=SBCL+HCL	5.40E+13	0.0	5000.0
18.	SBCL2+OH=SBCL+HOCL	1.50E+13	0.0	5500.0
19.	SBCL2+O=SBCL+CLO	1.80E+13	0.0	20000.0
20.	SBCL2+CL=SBCL+CL2	8.00E+12	0.0	21000.0
21.	SBCL+H=SB+HCL	3.00E+13	0.0	4500.0
22.	SBCL+OH=SB+HOCL	1.50E+13	0.0	23000.0
23.	SBCL+O=SB+CLO	4.00E+13	0.0	15000.0
24.	SBCL+CL=SB+CL2	7.00E+12	0.0	20500.0
25.	SBCL+H=SBH+CL	5.00E+12	0.0	15500.0
26.	SBCL+OH=SBO+HCL	5.90E+12	0.0	6500.0
27.	SBCL+O=SBO+CL	7.20E+13	0.0	6500.0
28.	CLSBO+H=SBO+HCL	1.50E+13	0.0	7500.0
29.	CLSBO+O=SBCL+O2	3.50E+12	0.0	9000.0
30.	SBCL+O+M=CLSBO+M	2.00E+16	0.0	0.0
31.	SBO+CL+M=CLSBO+M	1.00E+16	0.0	0.0
32.	SBCL+OH=CLSBO+H	2.00E+12	0.0	11000.0
33.	SBCL+CH3O=CLSBO+CH3	2.30E+12	0.0	8000.0
34.	SBCL+SBO=CLSBO+SB	8.00E+11	0.0	7500.0
35.	SBCL+SBO2=CLSBO+SBO	1.50E+12	0.0	7000.0
36.	SBO+CL2=CLSBO+CL	1.00E+13	0.0	5500.0