

CREATING A DETAILED MODEL FOR BORON NITRIDE DEPOSITION MECHANICS

Andrianna Daniels

Advisor: Harsha Chelliah

Mechanical & Aerospace Engineering Department

University of Virginia, Charlottesville, VA 22903

Abstract

This work ultimately sets out to create a validated mechanism to model the deposition of boron nitride films in low pressure chemical vapor deposition reactors. A model proposed by Mark Allendorf et al. at Sandia National Laboratories, published in 1996 acts as a starting point for an expanded model. The program Reaction Mechanism Generator (RMG) from MIT is being used to theoretically expand the model. Boron will be added into this program to achieve this goal. The Gaussian program is also used to generate

thermochemical data for various intermediate species that is required for RMG. First, a boron carbide model is generated to assess accuracy of results from RMG, replicating and expanding upon work done in 2022 by Dr. Vijay Shinde (IIT). After, an expanded boron nitride mechanism is created. The model will be validated experimentally with a micro-chemical vapor deposition reactor used in tandem with a gas chromatograph to sample species data within the reactor at various initial conditions. This work remains ongoing.

Introduction

It is well documented that ceramic matrix composite (CMC) materials, especially those based on carbon and/or silicon-carbide fibers, offer some of the highest strengths at temperatures over 1000 °C (Fig. 1), but issues occur with crack formation at fiber-matrix interfaces and the subsequent oxidation and corrosion of CMCs. This has posed major issues with reliability at high temperatures like those of relevance for NASA applications. One solution to this problem is to coat these composite materials with an interface material to allow for increased flexibility and slip between different fiber tows, and generally act as a reinforcement to the matrix.² One common interface coating that has been studied in previous literature is boron nitride (BN).^{2,3} BN is a good interface material candidate because it forms a weak mechanical bond and has minimal reactions with many CMCs (high chemical inertness).² This prevents the BN from damaging the CMC while providing the overall matrix increased flexibility and toughness. While BN has been shown to increase survivability of CMCs, no current mechanisms exist that model the formation of BN and/or BN intermediate species.

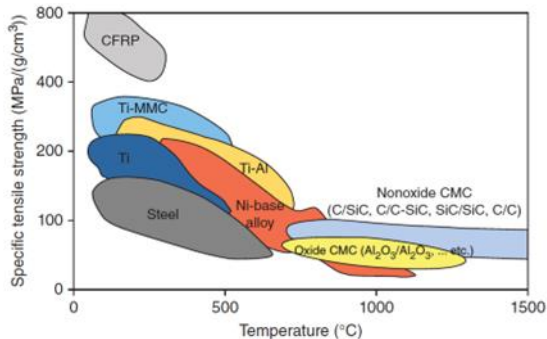


Figure 1: weight specific strength materials as a function temperature.¹ (adapted from Ref. 1)

The main method of forming BN films is via Chemical Vapor Infiltration (CVD). As BN and

doped-BN films are becoming more common, it is becoming increasingly necessary to understand and model the flow compositions that exist in a variety of reactor conditions to maximize production of such films and increase the film quality, therefore saving time and resources. A detailed model would also help researchers understand the many intermediate reactions that play a role in BN deposition.

Literature Review

Currently, there is one published, semi-global mechanism detailed in Allendorf et al. This model contains 11 reactions pertaining to BN formation via boron trichloride (BCl_3) and ammonia (NH_3).⁴ This model is shown in Figure 2. These two species are common precursors to BN formation, and have been used for BN deposition since the 1960s.⁵⁻⁹ Despite the large number of applications and studies of BN for the last 80 years, the Allendorf model remains the only published mechanism of any size. Some reaction rates were also estimated in the high-pressure limit for increased accuracy, though BN is typically grown in low-pressure CVD reactors. The paper also notes that many important reactions and species may have been left out of the mechanism due to the limited information available for certain species. In particular, BHCl_2 was one such species with potential importance that was intentionally excluded from the model.

Other mechanisms related to BN (i.e., pertaining to elements B-Cl-N-H and BCl_3/NH_3 decomposition) have also been proposed and tested. Though Allendorf's model predicts that BCl_3 decomposition by itself is largely negligible at common CVD reactor conditions (less than 5% decomposition

below 1400K with one second residence time),⁴ such pathways may become more

can be used with a CVD reactor to measure actual species concentrations within any range

	Reaction	$\Delta H_{\text{react}}^{\circ}$ ^f	A ^h	E_a	Notes
1.	$\text{Cl}_3\text{BNH}_3 \leftrightarrow \text{BCl}_3 + \text{NH}_3$	24.0	--	--	f
2.	$\text{Cl}_3\text{BNH}_3 \leftrightarrow \text{Cl}_2\text{BNH}_2 + \text{HCl}$	11.1	--	--	f
3.	$\text{BCl}_3 + \text{NH}_3 \leftrightarrow \text{Cl}_2\text{BNH}_2 + \text{HCl}$	-12.9	1.66E+12	19.9	a,b
4.	$\text{Cl}_2\text{BNH}_2 \leftrightarrow \text{ClBNH} + \text{HCl}$	56.0	3.89E+14	79.0	a,b,c
5.	$\text{Cl}_2\text{BNH}_2 + \text{NH}_3 \leftrightarrow \text{BCl}(\text{NH}_2)_2 + \text{HCl}$	-3.9	1.66E+12	19.9	a
6.	$\text{BCl}(\text{NH}_2)_2 + \text{NH}_3 \leftrightarrow \text{B}(\text{NH}_2)_3 + \text{HCl}$	6.9	1.66E+12	19.9	a
7.	$\text{BCl}_3 \leftrightarrow \text{BCl}_2 + \text{Cl}$	117.7	9.86E+15	113.7	a,c,d
8.	$\text{BCl}_2 \leftrightarrow \text{Cl} + \text{BCl}$	79.7	2.25E+15	76.9	a,c,d
9.	$\text{BCl}_3 + \text{H} \leftrightarrow \text{BCl}_2 + \text{HCl}$	14.5	1.00E+14	12.0	a
10.	$\text{BCl} + \text{HCl} \leftrightarrow \text{BCl}_2 + \text{H}$	23.4	7.23E+13	24.2	e
11.	$\text{NH}_3 + \text{M} \leftrightarrow \text{NH}_2 + \text{H} + \text{M}$	109.1	2.50E+16	93.8	g

^a This work. ^b Transition state from Ref. [9]. ^c High-pressure limit. ^d Rate estimated by RRKM calculation. ^e Ref. [16]. ^f Ref. [9], kcal mol⁻¹, 298 K. ^g Ref. [11]. ^h Units: cm, sec, moles.

Figure 2: Semi-empirical gas-phase mechanism for BN from Allendorf et al.⁴

important at higher operating temperatures. A model proposed by Reinisch et al. describes reactions within a system of boron/hydrogen/chlorine/carbon.¹⁰ Select reactions from this model pertaining to B/H/Cl reactions may prove important in the expansion of current BN deposition understanding. Similarly, Shrestha et al. details reactions within a nitrogen/hydrogen/carbon/oxygen system.¹¹ In this case, reactions involving N/H can be used to help expand the model. Allendorf's model itself refers to the use of an expanded, 45 reaction and 11 species¹² model for the decomposition of NH₃ at high temperatures, though this mechanism itself was not explicitly reported in the Allendorf paper.

Methodology

To build a working mechanism to model BN deposition, both theoretical and experimental approaches are necessary. First, the theoretical model must be expanded upon to estimate species concentrations within CVD reactors, including the addition of new species and elementary reaction steps. Then, when predicted stable and measurable species are identified from the model, a gas chromatograph

of input parameters. Then, various reactions within the model can be tuned to better reflect the reality displayed within the CVD reactor. Once the model has been tested and validated, the model can be reduced to a one-step model for implementation into various CFD simulation software.

To expand the available model, the open-source program Reaction Mechanism Generator (RMG), developed by Willaim Green's group at MIT, was used. RMG allows users to generate detailed kinetic models, comprised of elementary reaction steps. It uses fundamental thermochemical data (thermodata) and various kinetic theories.^{13, 14} The current version of RMG currently supports most first- and second-row periodic table elements, in addition to limited heavier elements, but it does not support the element boron. However, it's open-source nature allows it to be added by the user. This was demonstrated first by Dr. Shinde and coworkers.¹⁵ RMG relies on the general understanding of a species' electronic structure and general theory on how atoms and molecules react, and generates mechanisms

using thermodynamic, transport, and kinetic data sets.

Specific kinetic libraries (or subsets of reaction libraries) can be used to start/build a model, but this is not required. Kinetic families are how RMG ‘learns’ to generate new reactions applicable to a given set of input conditions. It can extrapolate from the input reaction family to form new reactions. The accuracy of these reactions can vary, but RMG is meant to be used iteratively, where initial models begin to point in the correct direction for a mechanism, and then more accurate thermodata and reaction parameters can be calculated using external software, input into RMG, and a new model with increased accuracy thus generated.

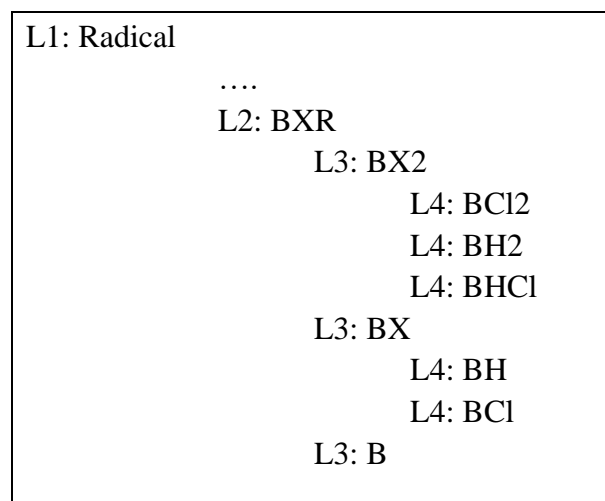


Figure 3: Possible tree structure addition for radical boron species, with similarly bonded species nesting together.

RMG also stores species thermodata in a tree-like structure, an example of which is given in Figure 3. This structure organizes and groups species onto various ‘limbs’ and ‘branches’ according to their bond characteristics (for example, nesting all of the two-bond boron species under BX_2 limb). Species are also grouped by stability, with stable species being denoted under the “group.py” file and radical species under the “radical.py” file. For any

species not coded into RMG but predicted by the program, Benson group additivity theory¹⁶ can be used, in addition to the identification of similar species from the tree structure, to estimate thermodynamic properties.

Boron Carbide Model Generation

In corresponding with Dr. Vijay Shinde, the methodology required to add boron into the RMG program was obtained. First, the code was tested by generating a unique theoretical boron carbide kinetic model for a set of parameters related to general CVD operational conditions. This was to ensure that boron was correctly added into the program. Second, an attempt to recreate the model results from Dr. Shinde’s group in Gupta et al. was done. This work was presented at the AIAA SciTech 2024 Conference in Orlando, FL and is detailed in Daniels et al.¹⁷ The work is summarized below.

Model Case 1:

First, a generic CVD model was generated. The physical conditions input into RMG were a temperature of 1300K and a pressure of 1 atmosphere. Initial species mole fractions were $BCl_3 = 0.01$, $CH_4 = 0.01$, and $Ar = 0.98$. From this model, the time-evolving composition of this system was calculated by integrating coupled sets of ODEs using the CANTERA reacting flow solver code. The initial conditions were the same as input into RMG.

As seen in Figure 4, the net reaction rate for BCl_3 sees a maximum at 0s with a slow decay thereafter. The intermediate species, especially CH_3 , HCl , and $BHCl_2$, continue to increase. This is because the model stops short of including heterogeneous surface reactions for the ultimate formation of BC , so there is no sink for these intermediate species. The eventual inclusion of surface reactions can

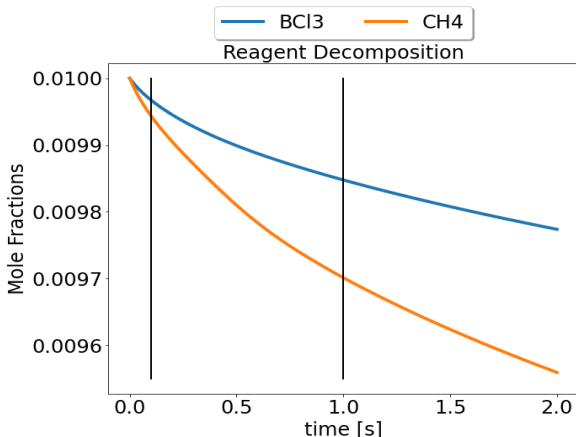


Fig. 4: Decomposition of BCl_3 and CH_3 at 1300K and 1 atm as predicted by a preliminary reaction mechanism for BC generated from RMG.

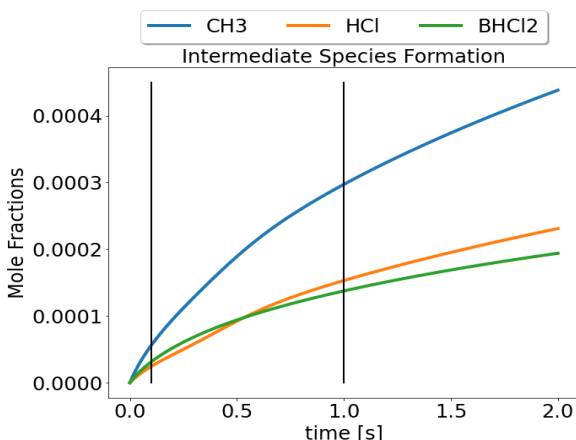


Fig. 5: Major species formed by BCl_3 and CH_3 at 1300K and 1 atm as predicted by a preliminary reaction mechanism for BC generated from RMG.

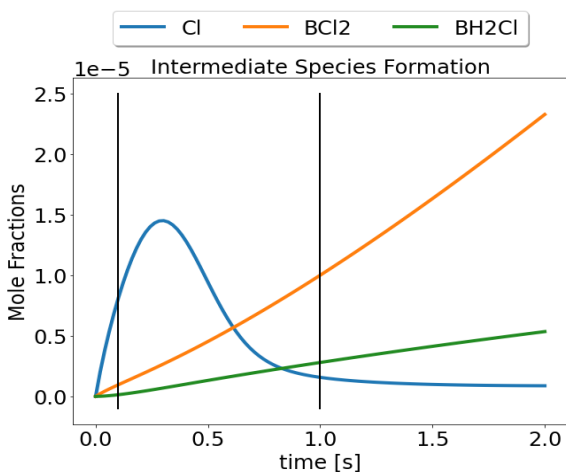


Fig. 6: Minor species formed by BCl_3 and CH_3 at 1300K and 1 atm as predicted by a preliminary reaction mechanism for BC generated from RMG.

drastically effect the predicted intermediate species concentration profiles. The location or time evolution of peak concentrations for key intermediate species can be used to optimize reactor designs and layouts in order to maximize BC deposition. In Figs. 4-6, two timesteps are denoted by black vertical lines, one at 100ms and another at 1s.

In addition to the time-evolving species concentrations, flux analyses of the reactions were computed for each element at two timesteps, 100ms and 1s. Here, the pathways for boron (Fig. 7a,b) and chlorine (Fig. 7c-d) are presented. The fluxes are normalized such that the largest flux on each pathway is 1.

From the pathway analyses like those shown in Fig. 7, dominant pathways can be identified, and measurable species along such pathways selected for experimental validation. By comparing the pathways at different time steps, it can be seen that more species form as the reactions evolve in time. For boron, in Fig. 7a to 7b, it's seen that most boron is predicted to form BHCl_2 at 100ms, but later at 1s more decomposition to BCl_2 is seen in addition to the formation of a new species BH_3 . For chlorine, Fig. 7c shows only small amounts of HCl decomposing to Cl atoms, but at the 1s timestep this pathway reverses. The overall flux of the chlorine atoms instead form molecular HCl. This trend is reflected in Fig. 6, with the peak Cl concentrations occurring around 400ms before decreasing thereafter.

Model Case 2:

After confirming the correct inclusion of boron into RMG with the first case, the flow reactor conditions used to validate the Shinde model were used to generate a new model. The Shinde model included optimization using experimental data from Reinisch et al.^{15,18} This model sought to recreate the work done in

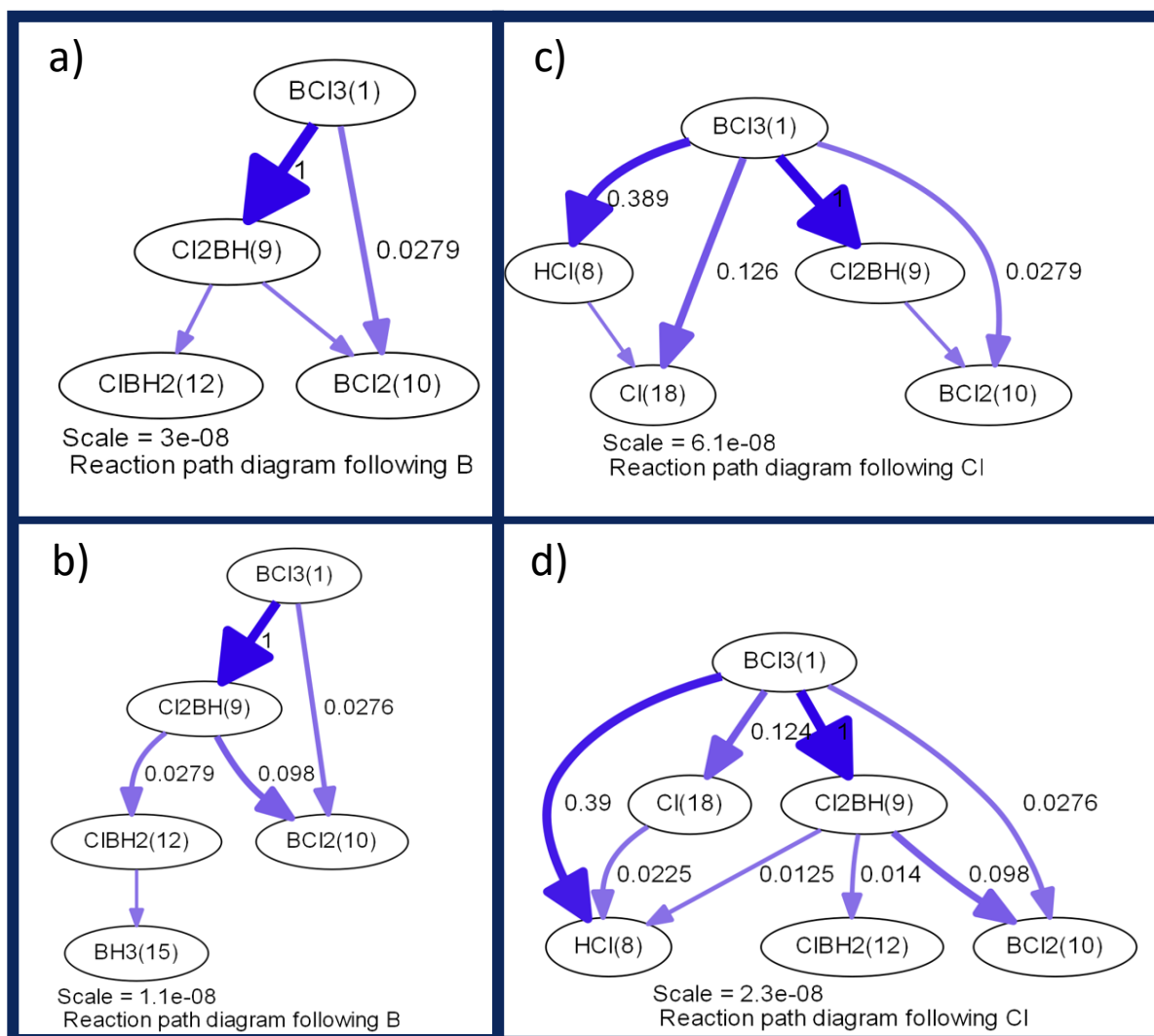


Fig. 7: Flux diagrams following a) B at 100ms b) B at 1s c) Cl at 100ms and d) Cl at 1s

Gupta et al. The conditions in each of these papers corresponded to $\text{BCl}_3 = 1.0$ moles, $\text{CH}_4 = 0.5$ moles, $\text{H}_2 = 5.0$ moles, $T = 1300\text{K}$, and $P = 12$ kPa. Note that this pressure is much lower than 1 atm (101.325 kPa) used in the first case.

A second key distinction was the residence time used for the analysis of the flow reactor. In Reinisch et al.¹⁸ experiments, the flow

reactor had a significant ramp up and ramp down temperature profile before and after the defined hot section of the reactor. This caused some ambiguity with the true effective hot-section of the reactor, thus leading to ambiguity in the overall residence time. In discussing with Dr. Shinde about his previous work, a residence time of about 3 seconds was estimated given the available parameters in the paper.

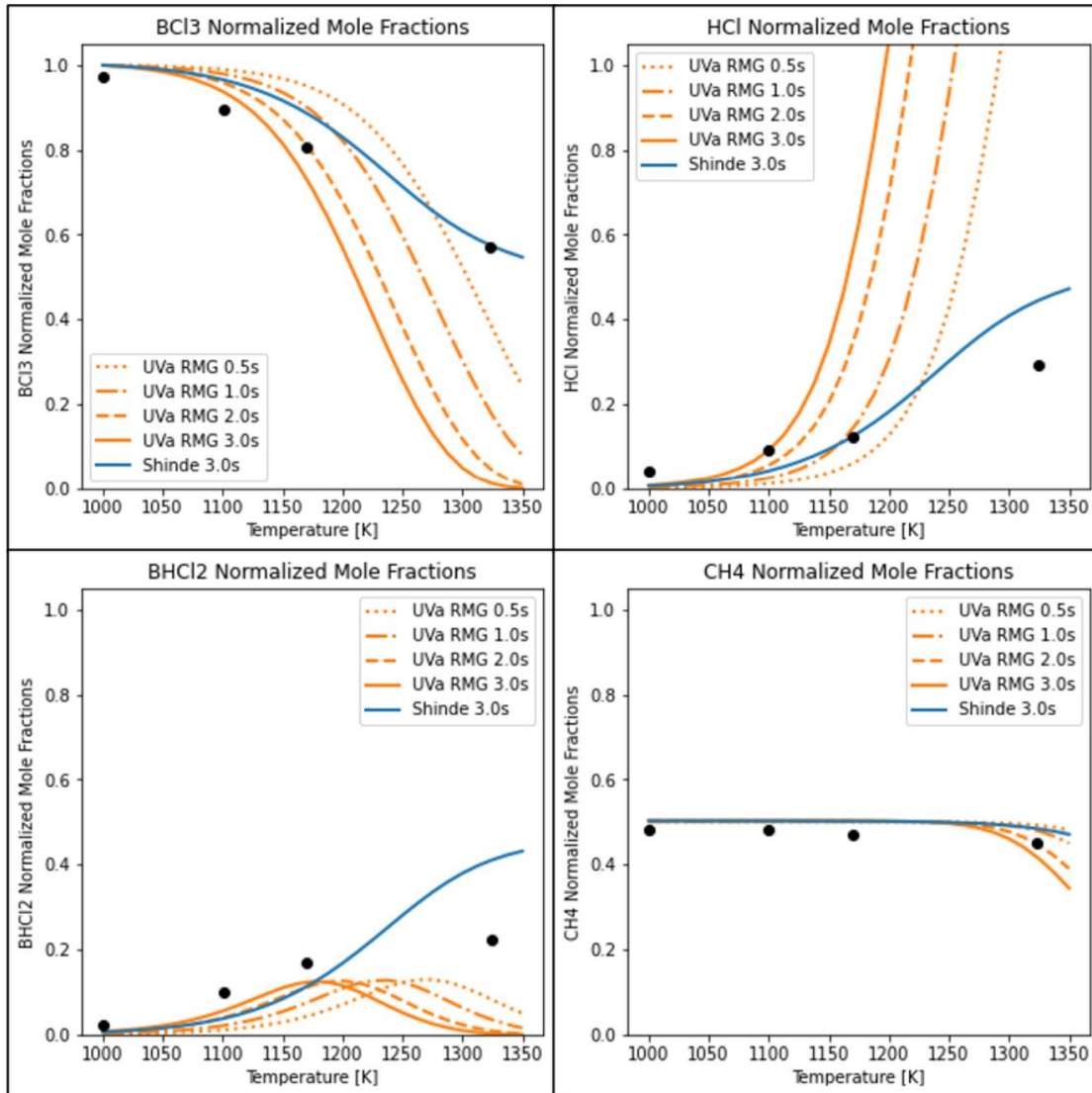


Fig 8: Normalized mole fraction comparisons between the UVa RMG model and Shinde model for BC deposition for species: a) BCl_3 , b) HCl , c) BHCl_2 , and d) CH_4 .

A new model was generated using the aforementioned conditions. At these conditions, a model consisting of 37 species (including 4 inert default gases) and 240 reactions was developed. Since the system was heavily diluted with H_2 gas, a zero-dimensional reactor simulation at constant temperature and pressure was used. The Shinde reduced model, consisting of 15 species and 26 reactions (reduced from the original model of 79 species and 1035 reactions), was run at 3 seconds, and the UVa RMG model was run at 0.5, 1, 2, and

3 seconds as shown with the dotted, dot-dashed, dashed, and solid orange lines in Fig. 8, respectively. Here, mole fractions for BCl_3 , HCl , CH_4 , and BHCl_2 were normalized to the mole fraction of BCl_3 at 1000K for each respective data set, and are plotted against temperature. Black dots indicate experimental data from Reinish et al.¹⁸ that were pulled from Gupta et al.¹⁵

The initial trends predicted by the UVa RMG model generally follow similar trends as to

those predicted by the Shinde model. With no model optimization or reduction, the UVa RMG model does a reasonable job at a first attempt to recreate the Shinde model. The effect of residence time on predicted trends is highlighted by the UVa model, indicating the importance of knowing the correct temperature-time history. It is clearly seen that the UVa model predicts much faster decomposition of BCl_3 than the Shinde model. Considering that the Shinde model was initially much larger, with 79 species and 1035 reactions, observed differences may indicate missing reaction pathways in the UVa RMG model, especially at higher temperatures. Unfortunately, this larger, unreduced model was unavailable for comparison, requiring further investigation to resolve the observed differences between the models.

It can also be noted that, despite the similarities in the conditions used to generate the Case 1 model and the Case 2 model, one major difference between the two models is the dilutant gas used. In Case 1, argon was used to dilute the system, and in Case 2 hydrogen was used. At a 2 second residence time, and a temperature of 1300K, it can be seen that in Case 1, only about 3% of the BCl_3 has decomposed, whereas in Case 2 at these same conditions, over 90% of the BCl_3 is decomposed. This may indicate the importance of hydrogen gas in the decomposition of BCl_3 . This prediction could be investigated experimentally with a CVD reactor.

Boron Nitride Model Development

With the above success in generating expanded analysis on the boron carbide modeling effort, the Allendorf reaction mechanism was added into RMG as a library, and initial modelling of a boron-nitride system has been done. This work is currently not yet available for

discussion, but there has been success in using the Allendorf model to generate an expanded gas-phase model for a boron nitride model. This model is still in its early stages, and requires more accurate data and model regeneration to increase its accuracy. Once a more trusted model has been generated, it can be experimentally validated using identified stable species in the mechanism. This data will be gathered from the UVa micro-CVD reactor using steps outlined in the previous year's fellowship report, available on the VSGC website. Once an expanded BN deposition model has been generated and experimental speciation data collected, the model can be verified and tuned to more accurately reflect the experimental data. The model may then be reduced to a one- or two-step model for implementation into various fluid simulation software to better optimize large-scale reactor setups.

Conclusions

In conclusion, boron has been successfully added into the RMG program. Two models related to boron carbide deposition have been generated and analyzed to demonstrate the success of boron in RMG. Next, a preliminary model related to boron nitride deposition has been generated. Future work for this project will include continuing the development and accuracy of new boron nitride deposition models, gathering experimental data, and validating/optimizing a BN model.

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