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Theoretical Study of Reaction $BF_3 + BF$ ® $BF_2 + BF_2$

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Abstract

A gas-phase kinetic mechanism for the Ar/B/F/N/H system was developed to describe the chemistry present during the growth of boron nitride films in a CVD reactor. The gas-phase mechanism, initially, includes 26 species and 67 elementary reactions, but this mechanism was extended to a mechanism with 35 species and 1012 reactions. Rate constants for 117 elementary reactions were obtained from published experimental/theoretical data and those for the other 895 reactions should be estimated using transition state theory(TST). We developed a simple program to determine the reaction rate by using conventional transition state theory and also the thermodynamic properties of the species. The program prints out the reaction rate in the Arrhenius form ($k = A\,T^n \exp(-E_a/RT)$) over the temperature range of 200 – 4000K and also, if it is desirable, the thermodynamic properties (heat capacity, entropy and enthalpy) in the polynomial form for 200-6000K temperature range. The reaction rate and the polynomial form for the thermodynamic properties is used in the kinetic program as ChemKin to simulated the gas phase composition during the growth of boron nitride in a plasma torch experiment. The theoretical data is used to optimize the experimental conditions because films properties depend on complex interactions involving heat and mass transport and chemical kinetics.

Introduction

- *There has been considerable interest in recent years, in the growth of boron nitride thin films;*
- *Like carbon, boron nitride has different allotropes, the hexagonal (hBN) and cubic (cBN) phases;*
- *The hexagonal phase, although electrically insulating, has properties that are very similar to graphite while the cubic phase has properties comparable to diamond;*
- *There is little understanding of the chemical process which are involved in and which control the synthesis of either hBN or cBN from the vapor phase;*
- *Theoretical research found in the literature includes thermodynamic equilibrium calculations for mixtures involving B/F/N/H and B/Cl/N/H, as well as limited kinetics studies of the reactions between BCl_3 and NH_3.*

Kinetic Model

- *Thin film deposition $\Rightarrow$ chemical process*
  - *Chemical species*
    - *Thermodynamic Properties*
  - *Chemical reactions*
    - *Rate constants (Arrhenius form): A, n, E_a*
      - *Experimental, theoretical*
- *Bimolecular reaction between A and B producing C and D:*

$$A + B \underset{k_r}{\overset{k_f}{\rightleftarrows}} C + D$$

- *Rate constants in Arrhenius form:*

$$k_f = AT^n \exp\left(-\frac{E_a}{RT}\right) \qquad k_r = k_f K_c = k_f \left(\frac{RT}{V}\right)^{\Delta\upsilon} \exp\left(-\frac{\Delta S}{R}\right) \exp\left(\frac{\Delta H}{RT}\right)$$

Theoretical Rate Constant

- *Collision theory:*

$$A = s_{AB} v_{AB}$$

- *Transition state theory:*

$$k_{TST}(T) = \frac{k_B T}{h} \frac{Q_{X^+}}{Q_A Q_{BC}} \exp\left(-\frac{V_a^{G^+}}{RT} \right)$$

$$V_a^{G^+} = V^+ + \varepsilon_{ZPE}$$

$$\beta = \arccos\left[\frac{m_A m_c}{(m_A + m_B)(m_B + m_C)} \right]^{1/2}$$

Partition Function $Q = Q_{trans} Q_{rot} Q_{vib} Q_{elet}$

	Degrees of freedom	Partition Function	Magnitude order
Translation	3	$Q_{trans} = \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2}$	10^{33} m^3
Rotation – 2D	2	$Q_{rot-2D} = \left(\frac{8\pi^2 I k_B T}{\sigma_e h^2} \right)$	$10 - 10^2$
Rotation – 3D	3	$Q_{rot-3D} = \left[\frac{\sqrt{\pi}}{\sigma_e} \left(\frac{8\pi^2 I_m k_B T}{h^2} \right)^{3/2} \right]$	$10^2 - 10^3$
Vibration	$n = 3N - 5$ $n = 3N - 6$	$Q_{vib} = \prod_{i=1}^{n} \left[1 - \exp\left(-\frac{hc\nu_i}{k_B T} \right) \right]^{-g_i}$	$1 - 10^n$
Electronic	–	$Q_{elet} = \sum_{i=0}^{n} g_i \exp\left(-\frac{\varepsilon_i}{k_B T} \right)$	1

Minimum Energy Path – MEP

$$V_{MEP} = -\frac{AY}{1+Y} - \frac{BY}{(1+Y)^2}$$

$$Y = e^{\alpha(s-S_0)}$$

$$A = \Delta E_C = V_{MPE}(s = +\infty)$$

$$B = \left((2V^+ - A) + 2\left(V^+(V^+ - A)\right)^{1/2}\right)$$

$$S_0 = -\frac{1}{\alpha}\ln\left(\frac{A+B}{B-A}\right)$$

$$\alpha^2 = -\frac{\mu(\omega^+)^2 B}{2V^+(V^+ - A)}$$

$$V_a^{G^+} = -\frac{ay}{1+y} - \frac{by}{(1+y)^2} - c$$

$$y = e^{\alpha(s-s_0)}$$

$$a = \Delta H_0 = V_a^{G^+}(s = +\infty) - V_a^{G^+}(s = -\infty)$$

$$b = \left(\left(2V_a^{G^+} - a\right) + 2\left(V_a^{G^+}\left(V_a^{G^+} - a\right)\right)^{1/2}\right)$$

$$c = \varepsilon_{int}^{G}(s = -\infty)$$

$$s_0 = -\frac{1}{\alpha}\ln\left(\frac{a+b}{b-a}\right)$$

Tunneling Corrections

- *Wigner:*

$$k_{TST}^{W}(T) = \kappa(T)k(T)$$

$$\kappa(T) = 1 + \frac{1}{24}\left|\frac{\hbar\omega^{+}}{k_B T}\right|^2$$

- *Eckart:*

$$\kappa(E) = 1 - \frac{\cosh[2\pi(\alpha-\beta)] + \cosh[2\pi\gamma]}{\cosh[2\pi(\alpha+\beta)] + \cosh[2\pi\gamma]}$$

$$\alpha = 1/2\sqrt{E/C} \qquad \beta = 1/2\sqrt{(E-a)/C}$$

$$\gamma = 1/2\sqrt{(b-C)/C} \qquad C = \frac{\left(h\omega^{+}\right)^2 B}{16\Delta V^{+}\left(\Delta V^{+} - a\right)}$$

$$\Gamma(T) = \frac{\exp\left(\Delta V^{+}/RT\right)}{RT}\int_0^{\infty}\exp(-E/RT)\kappa(E)dE$$

Thermodynamic Properties

$$A = -k_B T \ln Q$$

$$G = A + PV$$

$$E = k_B T \left(\frac{\partial \ln Q}{\partial \ln T} \right)_v$$

$$H \equiv E + PV$$

$$S = k_B \ln Q + k_B \left(\frac{\partial \ln Q}{\partial \ln T} \right)_v$$

$$C_v = \frac{k_B}{T^2} \left(\frac{\partial^2 \ln Q}{\partial (1/T)^2} \right)_v$$

$$C \equiv C_v + R$$

$$\frac{c_p}{R} = \sum_{i=1}^{n} a_i T^{i-1}$$

$$\frac{H}{RT} = \frac{b_1}{T} + \frac{1}{RT} \int c_p dT$$

$$\frac{S}{R} = b_2 + \int \frac{c_p}{RT} dT$$

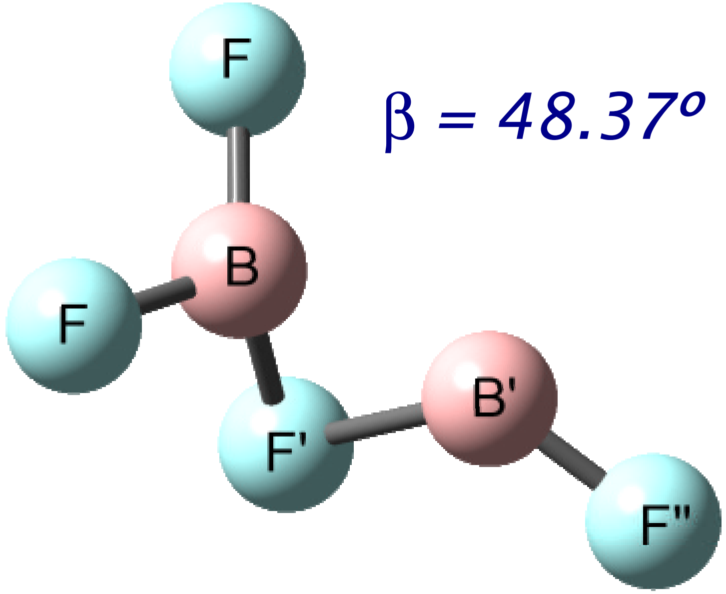
- Two temperature range
  - 0 – 1000 K
  - 1000 – 6000 K
- Seven coefficient

Optimized Geometry HF/6-31G(d)

	BF_3	BF	BF_2	$F_2BF'B'F''$
R_{BF}	1.324		1.321	1.382
$R_{BF'}$				1.500
$R_{B'F'}$				1.403
$R_{B'F''}$		1.281		1.251
A_{FBF}	120.0		121.1	117.770
$A_{FBF'}$				112.097
$A_{BF'B'}$				62.759
$A_{F'BF''}$				112.902

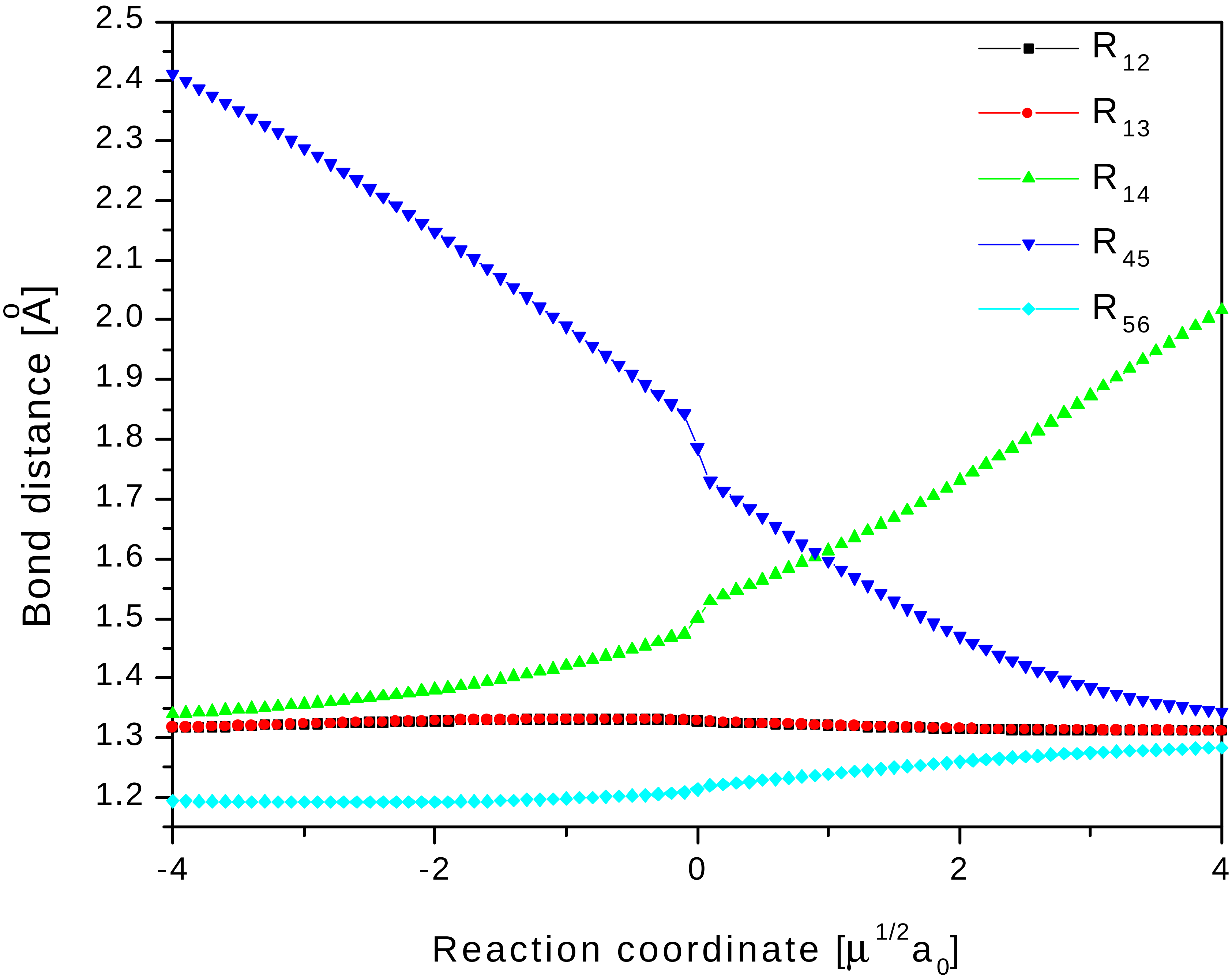
	BF_3	BF	BF_2	TS
	480.95	1471.09	522.85	138.99
	480.95		1173.66	278.88
	698.54		1446.56	366.99
	888.61			396.39
	1496.76			508.70
	1496.76			512.90
				686.76
				862.62
				1200.20
				1433.64
				1655.59
				427.92i
ZPE	8.357	2.103	4.178	11.496

BF_3	*-323.1954852*
BF	*-124.1031842*
BF_2	*-223.6268073*
TS	*-447.1987338*
Reaction Entalphy	*27.248*
Potential Barrier	*63.746*

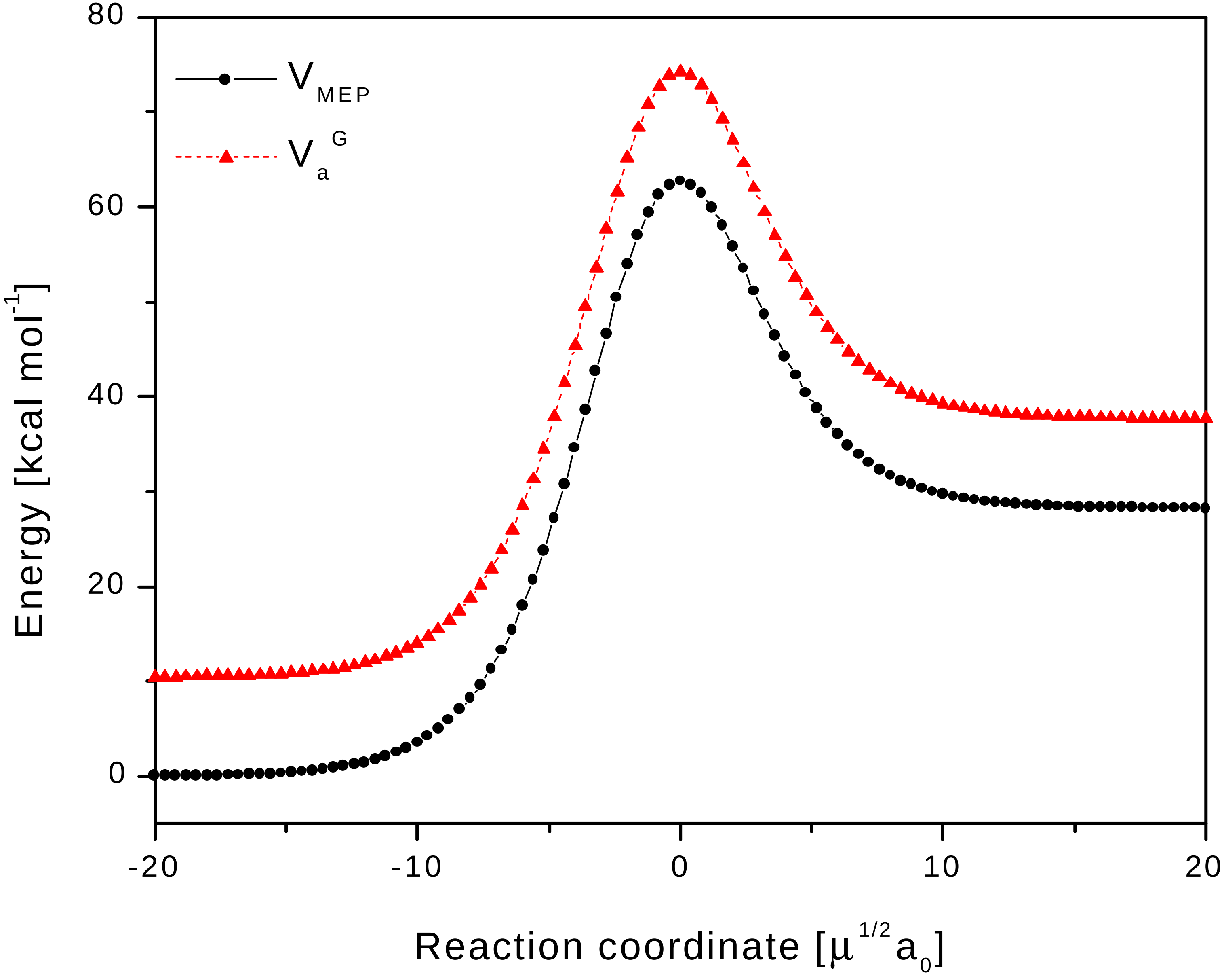


$\beta = 48.37^o$

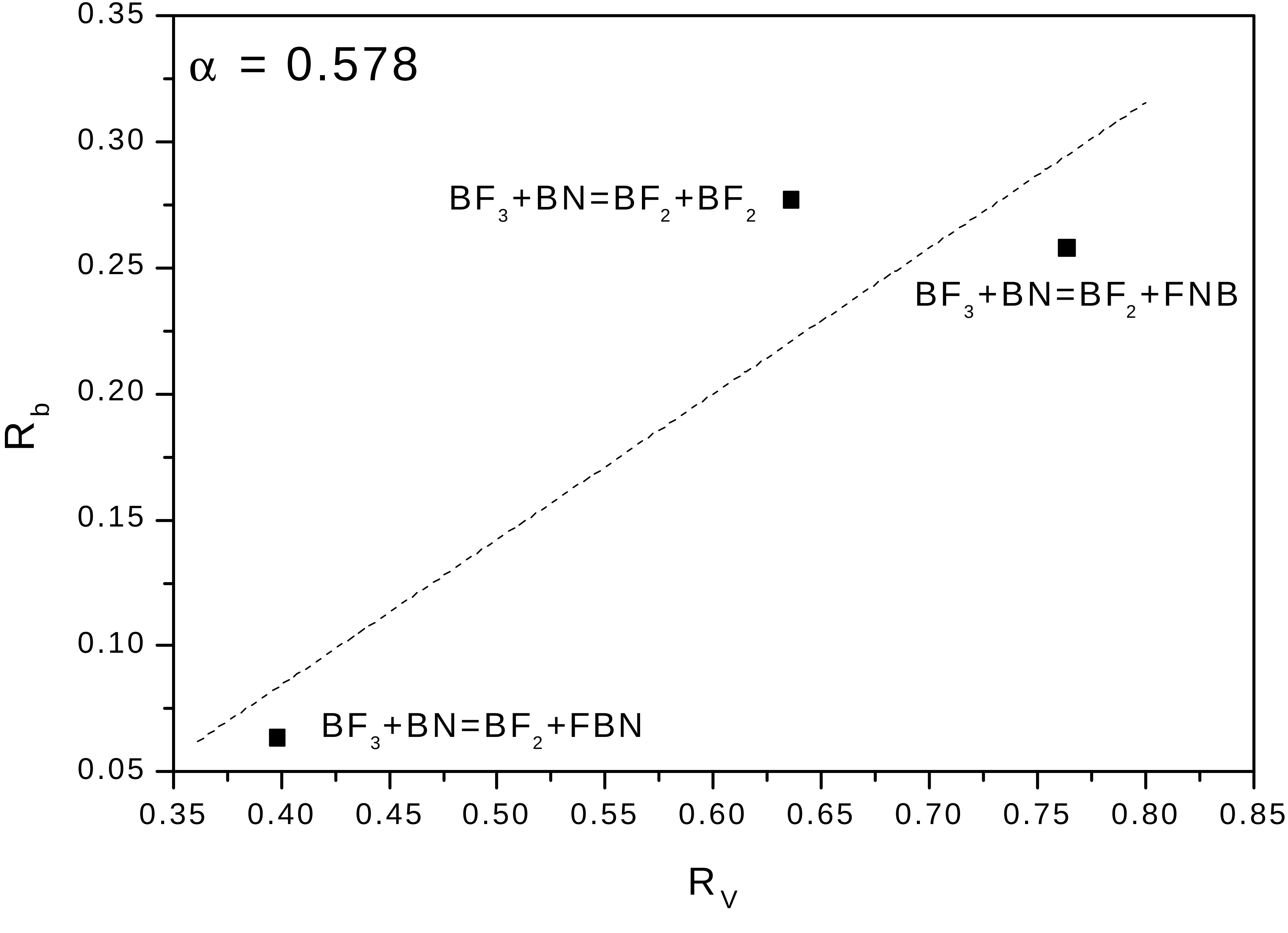
BF		BF_2		BF_3	
0.4341E+01	-.84896E+00	0.3832E+01	0.5156E+01	0.3109E+01	0.6933E+01
-.76199E-02	0.82593E-02	0.89619E-03	0.18512E-02	0.85572E-02	0.30749E-02
0.31068E-04	-.39087E-05	0.10616E-04	-.71641E-06	0.73393E-05	-.11890E-05
-.44477E-07	0.74485E-09	-.14939E-07	0.12138E-09	-.19342E-07	0.20134E-09
0.20884E-10	-.49851E-13	0.60000E-11	-.75098E-14	0.93432E-11	-.12453E-13
-.12010E+04	0.5899E+03	-.12487E+04	-.18368E+04	-.13349E+04	-.25889E+04
0.7233E+01	0.3485E+02	0.5059E+01	-.28983E+01	0.8633E+01	-.12207E+02



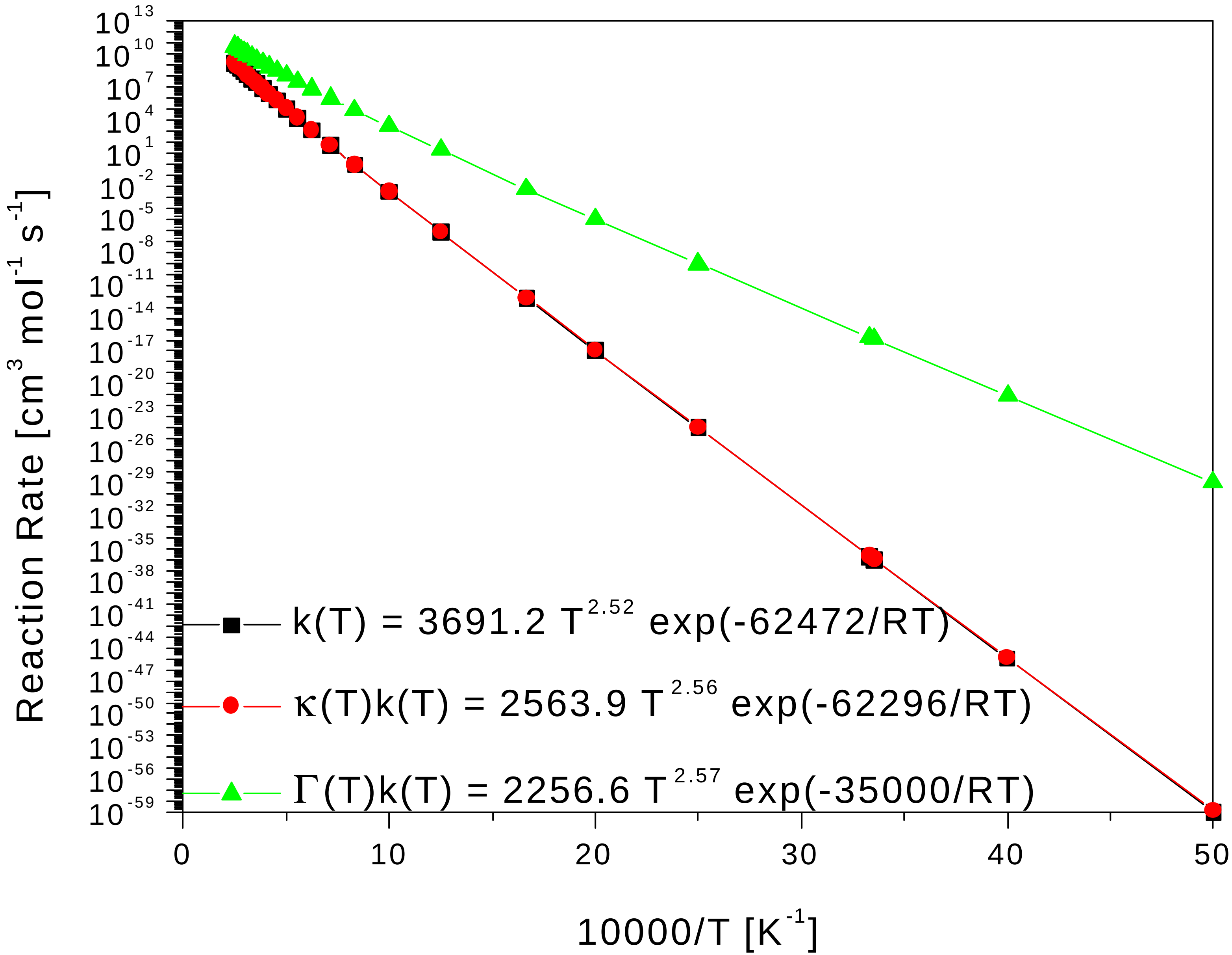
Bond distance [Å]
Reaction coordinate [μ^1/2 a0]
R 12
R 13
R 14
R 45
R 56
2.5
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
-4
-2
0
2
4



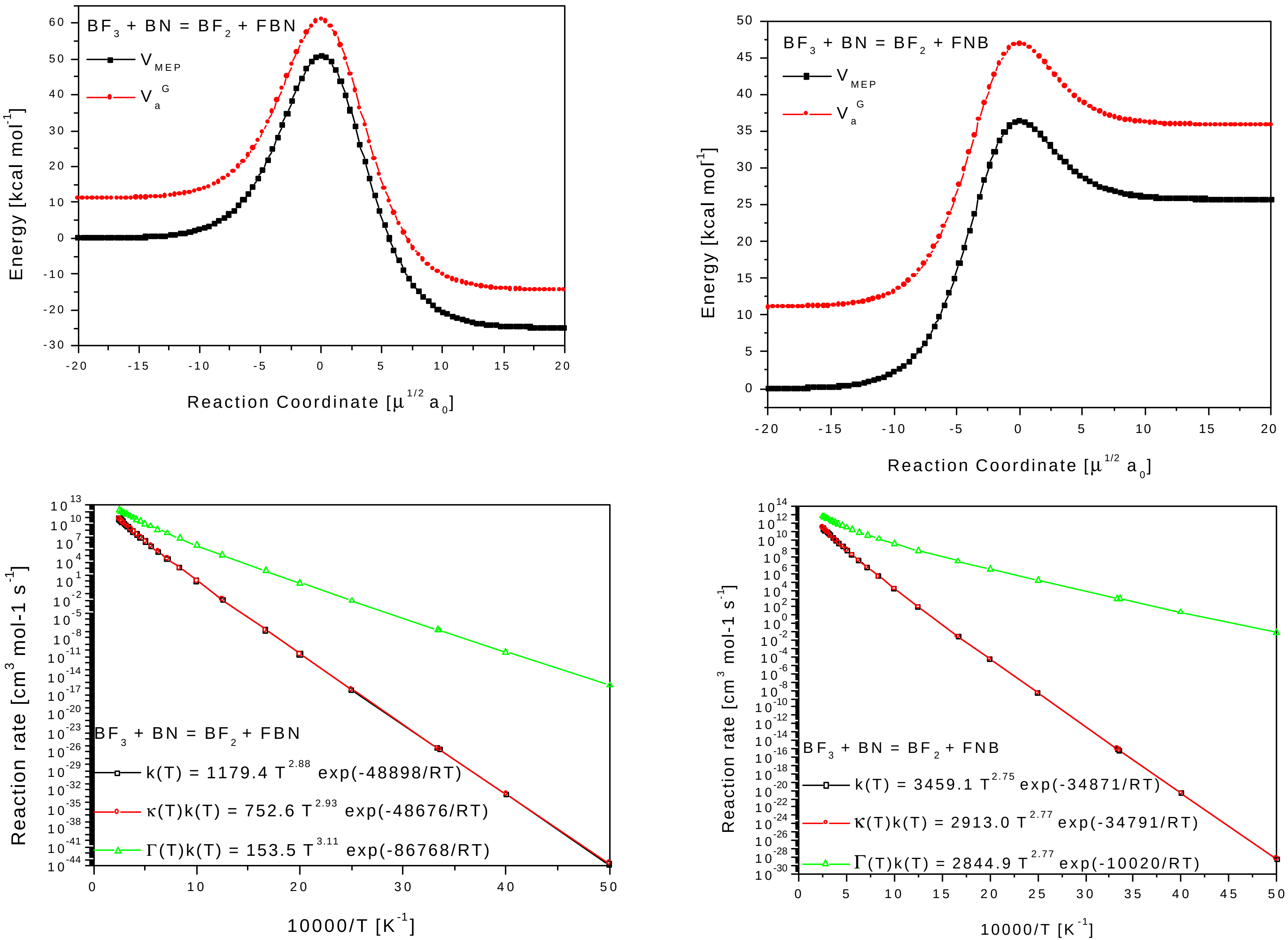
80
60
40
20
0
-20
-10
0
10
20
V_{MEP}
V_a^G
Energy [kcal mol^{-1}]
Reaction coordinate [$\mu^{1/2}a_0$]



α = 0.578
BF3+BN=BF2+BF2
BF3+BN=BF2+FNB
BF3+BN=BF2+FBN
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
Rb
RV



Reaction Rate [cm^3 mol^{-1} s^{-1}]
10000/T [K^{-1}]
$k(T) = 3691.2\ T^{2.52} \exp(-62472/RT)$
$\kappa(T)k(T) = 2563.9\ T^{2.56} \exp(-62296/RT)$
$\Gamma(T)k(T) = 2256.6\ T^{2.57} \exp(-35000/RT)$


BF3 + BN = BF2 + FBN
VMEP
Va G
Energy [kcal mol-1]
Reaction Coordinate [μ1/2 a0]
BF3 + BN = BF2 + FNB
VMEP
Va G
Energy [kcal mol-1]
Reaction Coordinate [μ1/2 a0]
BF3 + BN = BF2 + FBN
k(T) = 1179.4 T2.88 exp(-48898/RT)
κ(T)k(T) = 752.6 T2.93 exp(-48676/RT)
Γ(T)k(T) = 153.5 T3.11 exp(-86768/RT)
Reaction rate [cm3 mol-1 s-1]
10000/T [K-1]
BF3 + BN = BF2 + FNB
k(T) = 3459.1 T2.75 exp(-34871/RT)
κ(T)k(T) = 2913.0 T2.77 exp(-34791/RT)
Γ(T)k(T) = 2844.9 T2.77 exp(-10020/RT)
Reaction rate [cm3 mol-1 s-1]
10000/T [K-1]

Conclusion

We have studied the gas-phase BF_3 + BF ® $2BF_2$ abstraction reaction with the conventional transition state theory with the Wigner and the Eckart transmission coefficient using our own code. With these information, we calculated the reaction rate over a wide temperature range from 200-4000K. We found that the reaction rate obtained using conventional transition state, with or not the Wigner and Eckart transmission coefficient have the same behavior in the high temperature range,1000-4000 K, that we are interested in. Understanding the chemical process which are involved in and which control the synthesis of either hexagonal or cubic boron nitride from the vapor phase are the goal of our research. Furthermore, the results presented in this work could elucidate the BF_3 decomposition that is very important for the kinetic mechanism information of boron nitride using as BF_3, H_2 and N_2 as the gas source.