

# Theoretical Study of Reaction

$$\text{BF}_3 + \text{BH} \textcircled{R} \text{BF}_2 + \text{BHF}$$

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# Abstract

A kinetic mechanism describing the growth of boron nitride films was developed. The gas-phase mechanism includes 35 species and 1012 reactions and also extends a previous mechanism that contained 26 species and 67 elementary 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). In this work we present the rate constants for the title reaction. So, direct dynamic method was applied, which use information on equilibrium geometries, electronic structure energy, first and second energy derivatives calculated via electronic structure. With these information, the rate constant were calculated for the temperature range 200-4000K, using our own code.

# 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  $\text{BCl}_3$  and  $\text{NH}_3$*

# *Rate Constant*

$$k_{\text{TST}}(T) = \frac{k_{\text{B}}T}{h} \frac{Q_{\text{X}^+}}{Q_{\text{A}}Q_{\text{BC}}} \exp\left(-\frac{V_{\text{a}}^{\text{G}^+}}{RT}\right)$$

$$V_{\text{a}}^{\text{G}^+} = V^+ + \epsilon_{\text{ZPE}}$$

$$\beta = \arccos\left[\frac{m_{\text{A}}m_{\text{C}}}{(m_{\text{A}} + m_{\text{B}})(m_{\text{B}} + m_{\text{C}})}\right]^{1/2}$$

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

	Degrees of freedom	Partition Function	Magnetude order
Translation	3	$Q_{trans} = \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2}$	$10^{33} \text{ m}^3$
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	$n = 3N - 5$ $n = 3N - 6$	$Q_{vib} = \prod_{i=1}^n \left[ 1 - \exp\left( -\frac{h\nu_i}{k_B T} \right) \right]^{-g_i}$	$1 - 10^n$
Electronic	-	$Q_{elet} = \sum_{i=0}^n g_i \exp\left( -\frac{\epsilon_i}{k_B T} \right)$	1

# Minimum Energy Path – MEP

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

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

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

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

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

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

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

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

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

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

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

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

# Tunneling Corrections

➤ *Wigner:*  $k_{\text{TST}}^{\text{W}}(T) = \kappa(T)k(T)$

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

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

$$\alpha = 1/2\sqrt{E/C}$$

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

$$\gamma = 1/2\sqrt{(b - C)/C}$$

$$C = \frac{(\hbar\omega^+)^2 B}{16\Delta V^+ (\Delta V^+ - a)}$$

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

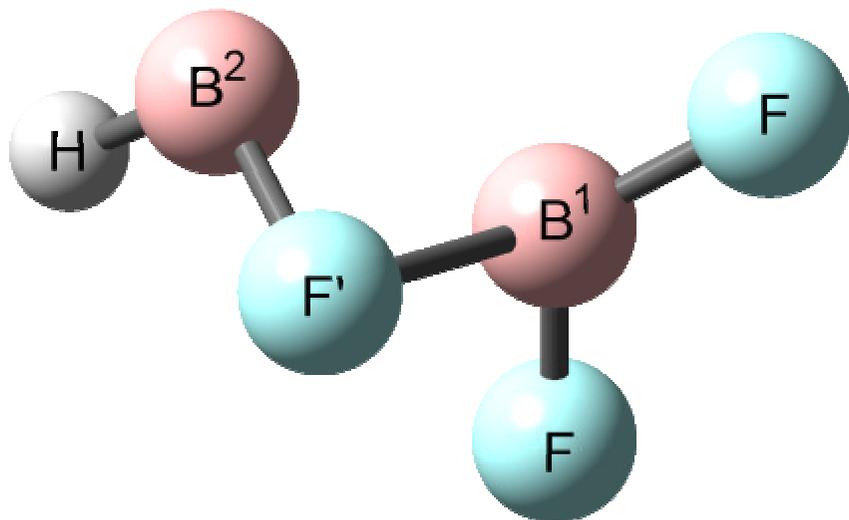
# Optimized Geometry

## HF/6-31G(d)

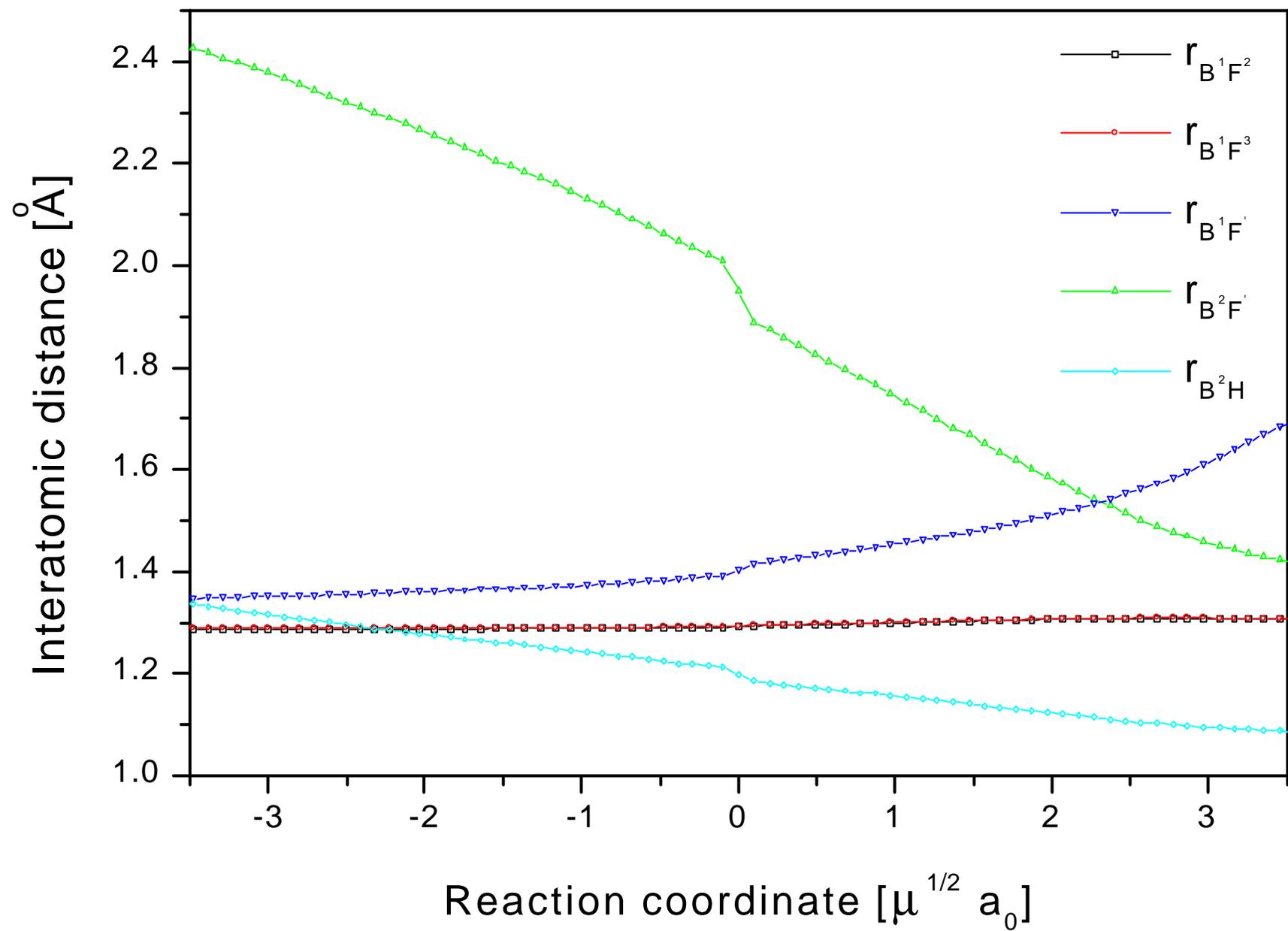
	$BF_3$	$BH$	$BF_2$	$BHF$	$F_2BF'B'H$
$R_{BF}$	1.324		1.321	1.319	1.294
$R_{BH}$		1.421		1.200	1.190
$R_{BF'}$					1.940
$R_{B'F'}$					1.403
$A_{FBF}$	120.0		121.1		123.42
$A_{FBF'}$					107.68
$A_{F'B'H}$				121.2	119.75
$A_{BF'B'}$					68.75

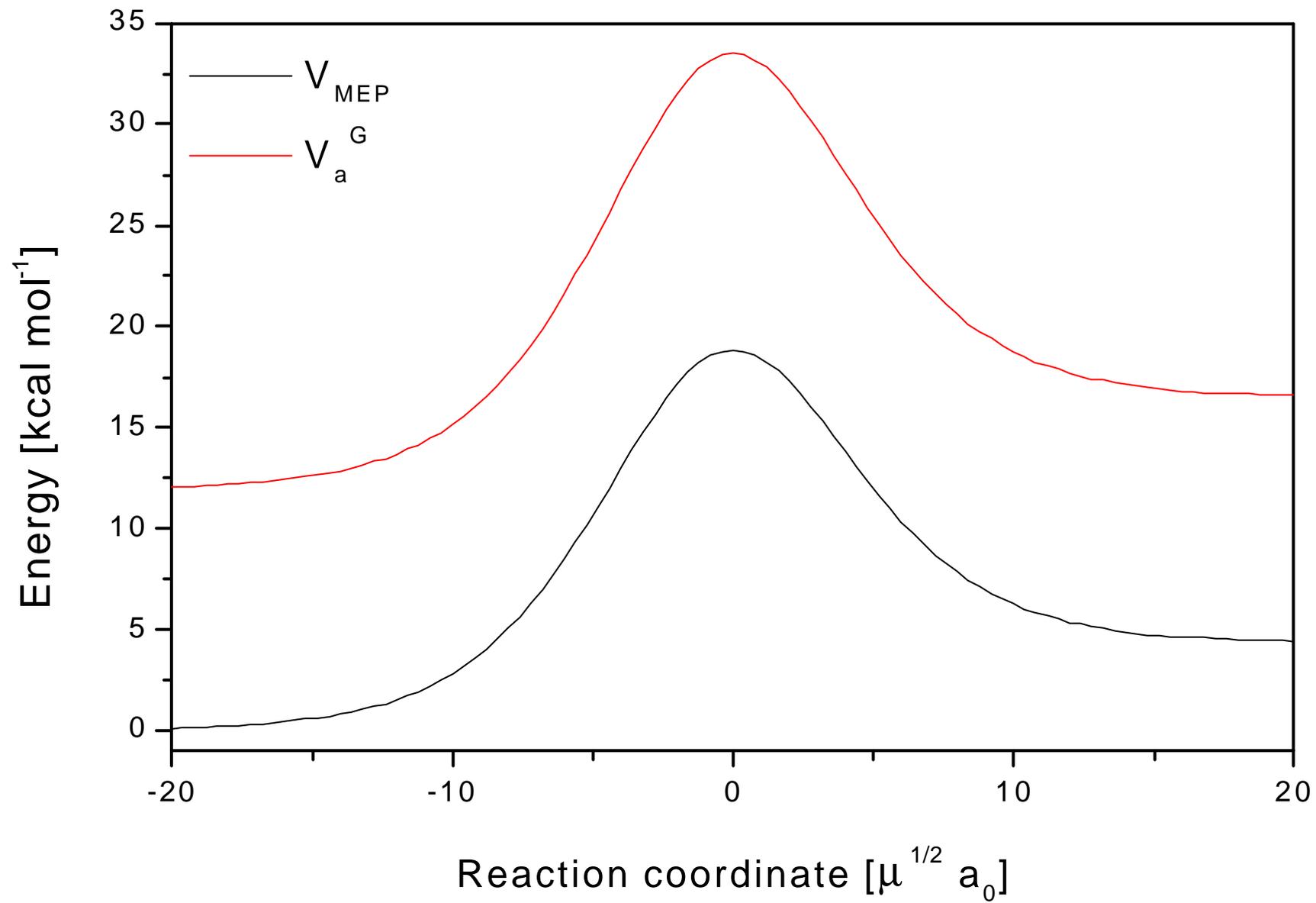
	$BF_3$	$BH$	$BF_2$	$BHF$	$BF_3BH$
	480.95	2511.20	522.85	1098.7	166.07
	480.95		1173.66	1388.7	248.11
	698.54		1446.56	2707.5	302.26
	888.61				461.76
	1496.76				603.51
	1496.76				803.48
					989.69
					1092.86
					1241.26
					1593.07
					2722.77
					192.71i
ZPE	8.36	3.59	4.72	7.43	14.64

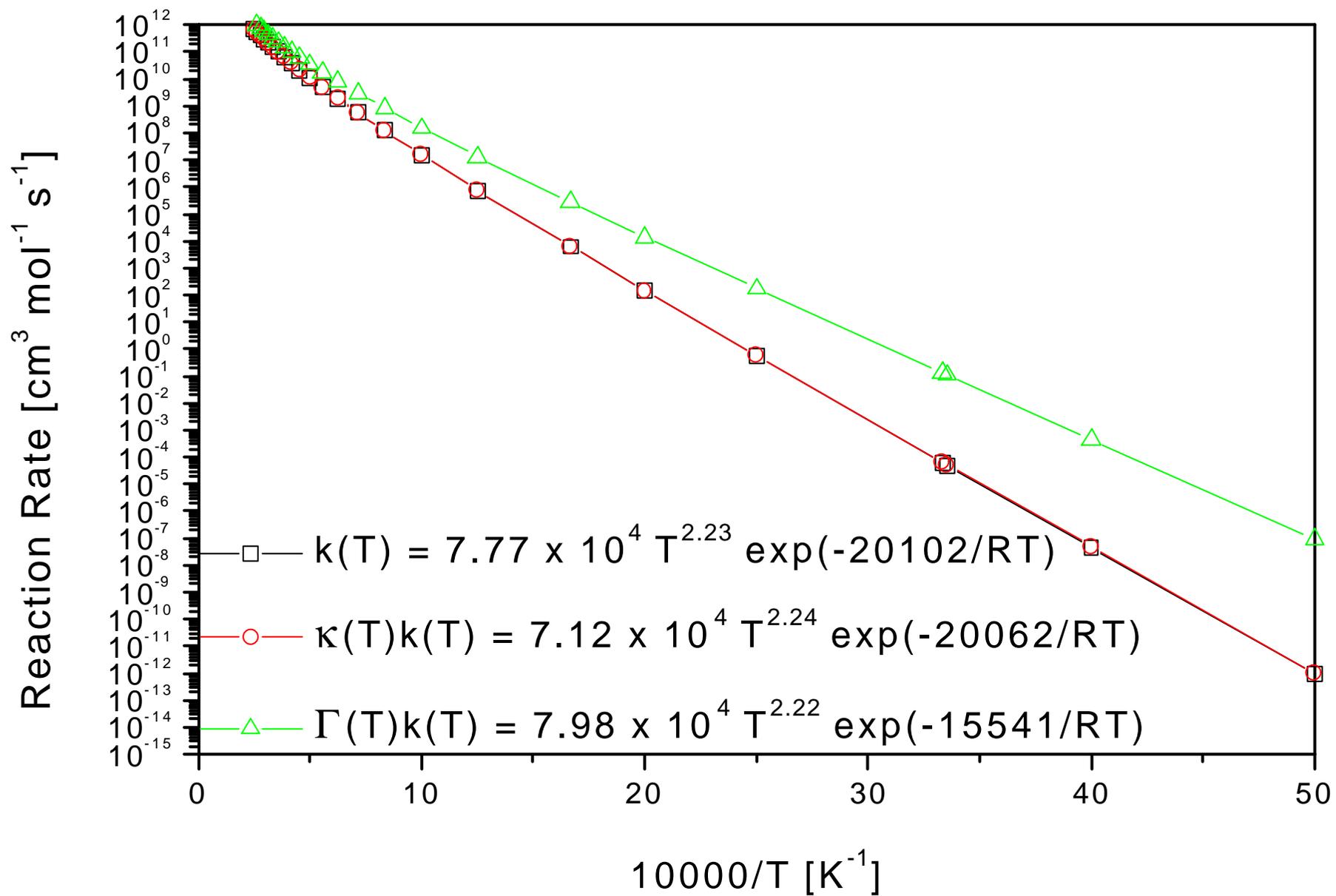
$BF_3$	-323.1954852
$BH$	-25.1182579
$BF_2$	-223.6268073
$BHF$	-124.6800233
$TS$	-348.2837118
<i>Reaction Entalphy</i>	4.536
<i>Potential Barrier</i>	21.540



$$\beta = 58.10^\circ$$







# Conclusion

We have studied the gas-phase  $\text{BF}_3 + \text{BH} \rightleftharpoons \text{BF}_2 + \text{BHF}$  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  $\text{BF}_3$  decomposition that is very important for the kinetic mechanism information of boron nitride using as  $\text{BF}_3$ ,  $\text{H}_2$  and  $\text{N}_2$  as the gas source.

