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Theoretical Study of Reaction BF_3 + BN

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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. In this work we discuss the results for the reactions BF_3 + BN. To study these reaction direct dynamic method was applied, which used information on equilibrium geometries, electronic structure energy, first and second energy derivatives calculated ab initio methods along the minimum energy path. 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 BCl_3 and NH_3*

Rate Constant

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

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

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

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

	Degrees of freedom	Partition Function	Magnetude 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

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

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

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

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

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

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

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

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

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

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

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

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

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:*

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

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

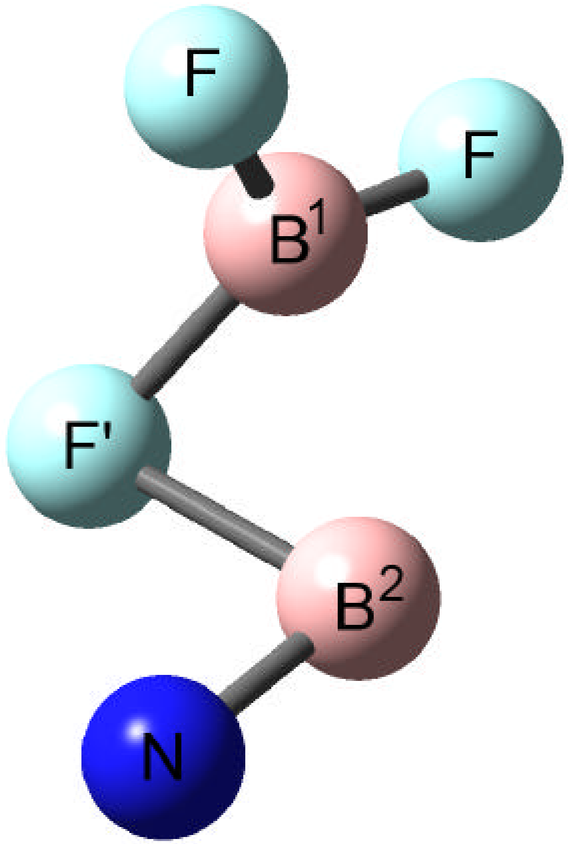
$$\gamma = 1/2\sqrt{(b-C)/C} \qquad C = \frac{(h\omega^{+})^2 B}{16\Delta V^{+}(\Delta V^{+} - a)}$$

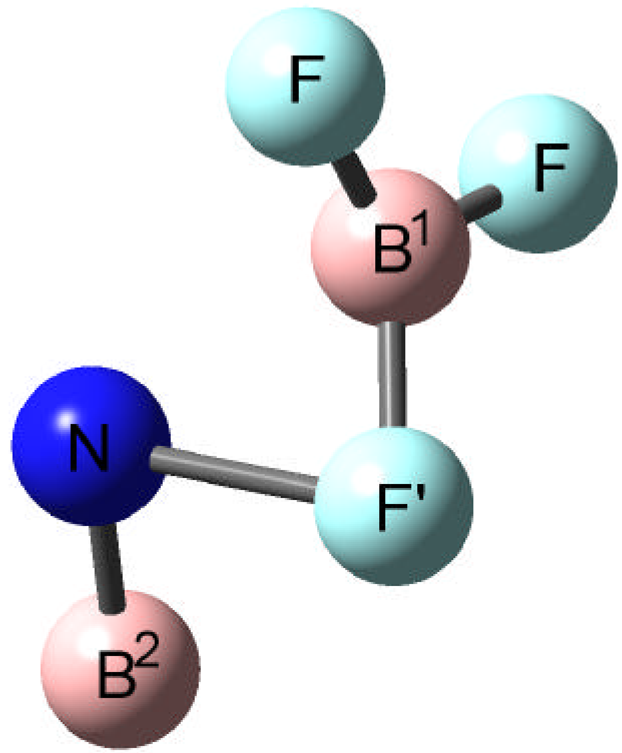
$$\Gamma(T) = \frac{\exp(\Delta V^{+}/RT)}{RT}\int_0^{\infty}\exp(-E/RT)\kappa(E)dE$$

Optimized Geometry HF/6-31G(d)

	BF_3	BN	BF_2	FBN	FNB	BF_3BN	BF_3NB
R_{BF}	1.324		1.321	1.290		1.299	1.301
R_{BN}		1.325		1.324	1.228	1.450	1.450
R_{NF}					1.320		
$R_{BF'-q}$						1.550	1.369
$R_{XF'-f}$						1.940	1.890
A_{FBF}	120.0		121.1			121.6	121.6
$A_{F'XY}$				180.0	180.0	92.4	96.2
$A_{FBF'}$						117.4	117.4

BF_3BN BF_3NB

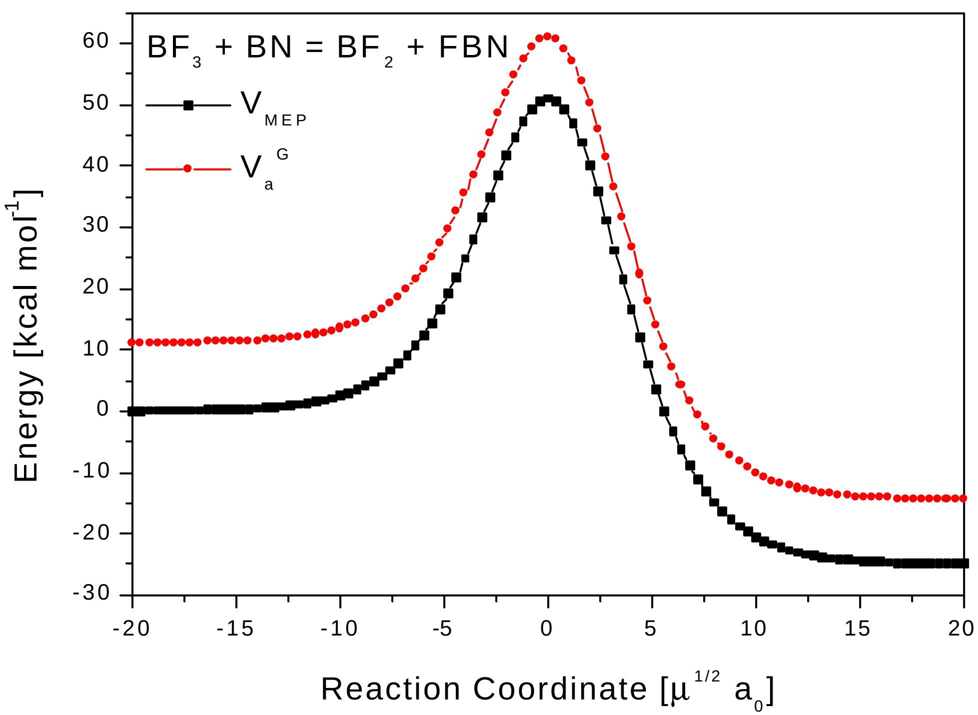


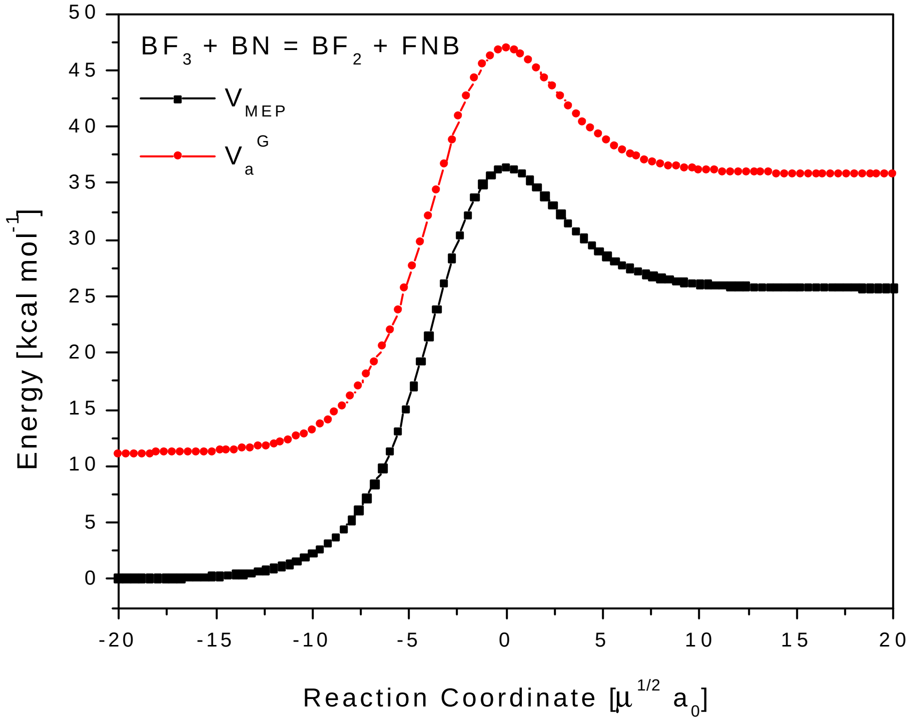


β = *50.21º*

BF_3	BN	BF_2	FBN	FNB	TS1	TS2
480.9	1890.3	522.9	222.8	462.5	174.7	89.2
480.9		1173.7	222.8	481.5	210.2	178.2
698.5		1446.6	1115.0	1050.0	263.3	228.8
888.6			2191.6	2024.1	310.4	334.1
1496.8					402.0	474.2
1496.8					430.6	499.9
					605.2	610.0
					654.7	875.5
					1141.8	1115.0
					1177.4	1385.9
					1587.7	1585.8
					489.4i	276.5i
8.36	2.70	4.72	5.74	5.36	9.95	10.54

	BF_3BN	BF_3NB
BF_3	-323.1954852	-323.1954852
BN	-78.9385726	-78.9385726
BF_2	-223.6268073	-223.6268073
FXY	-178.5470744	-178.4662358
TS	-402.0527453	-402.0761005
Reaction Entalphy	24.759	-25.587
Potential Barrier	35.855	49.911


BF3 + BN = BF2 + FBN
VMEP
Va G
Energy [kcal mol-1]
Reaction Coordinate [μ1/2 a0]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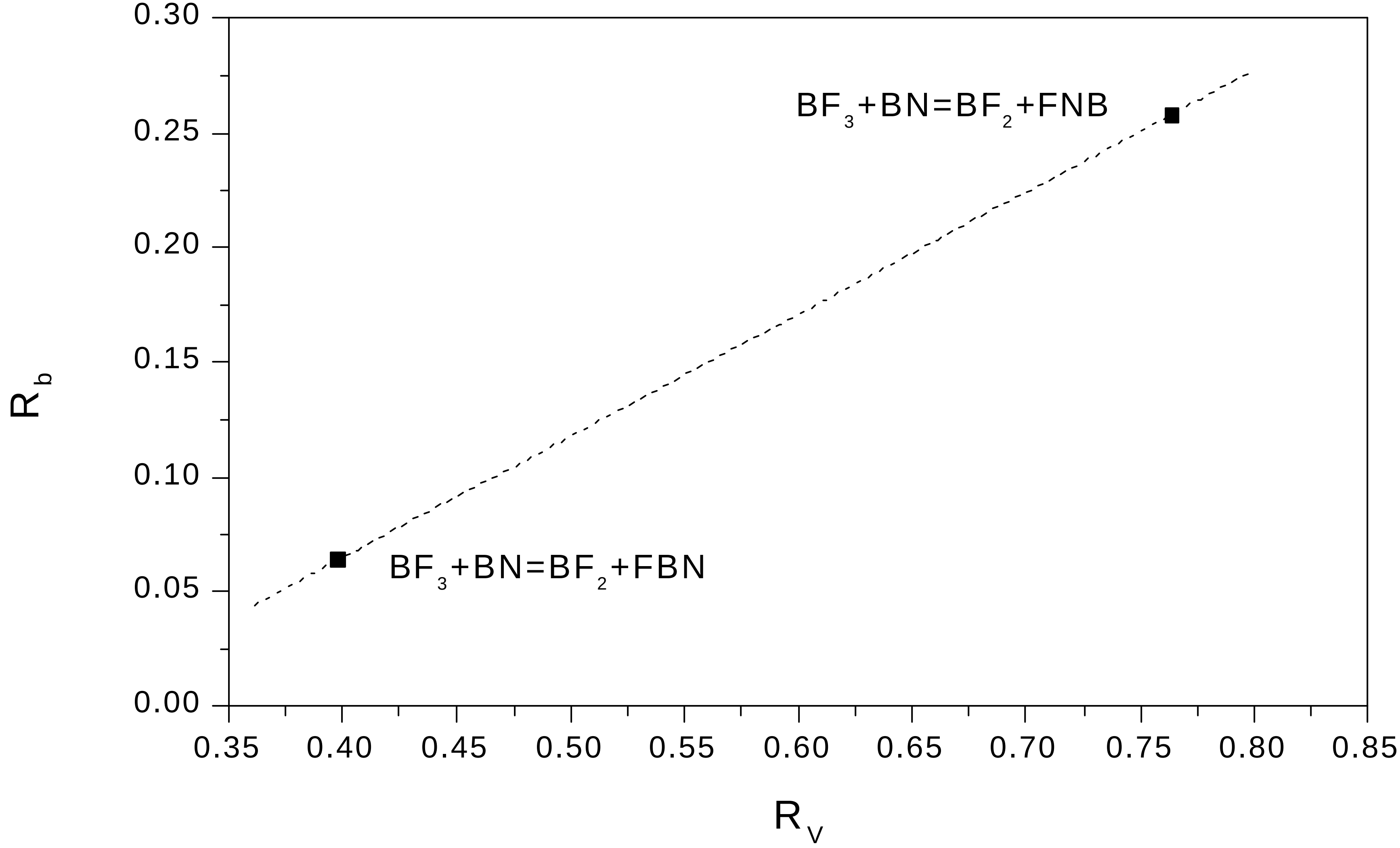
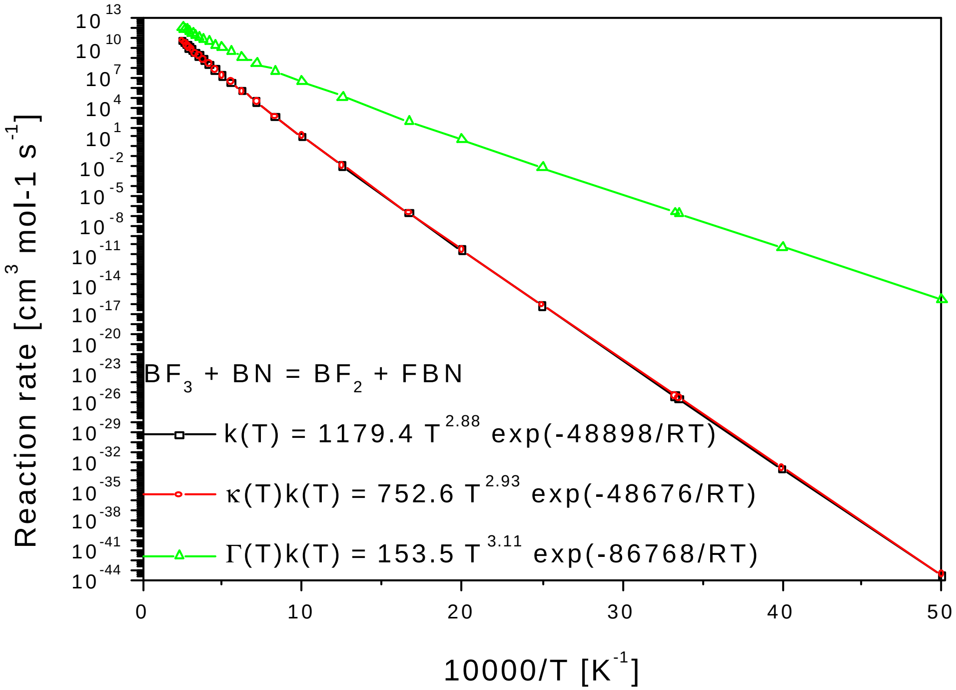
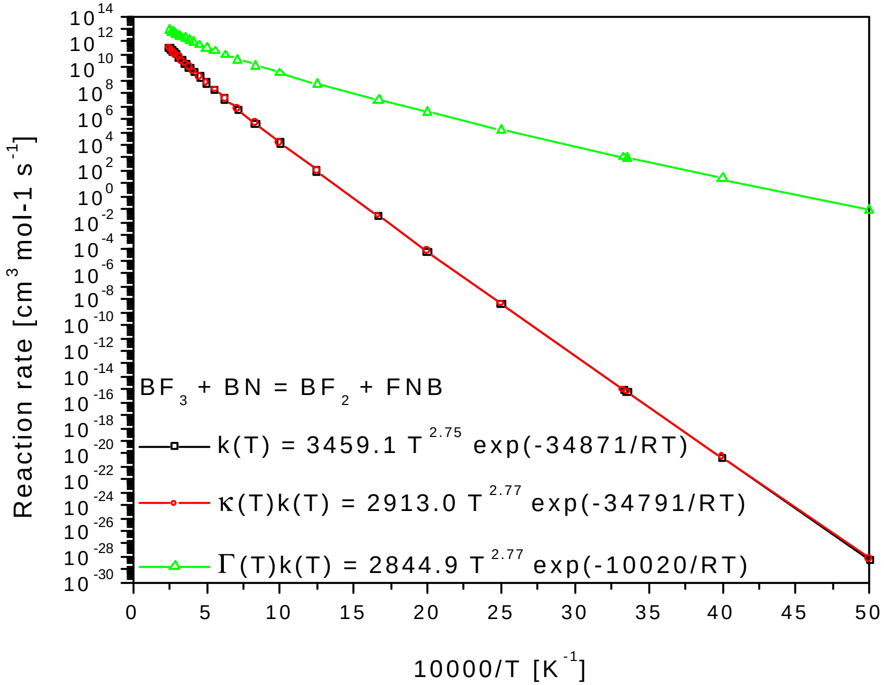


0.30
0.25
0.20
0.15
0.10
0.05
0.00
R_b
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
R_V
$BF_3+BN=BF_2+FNB$
$BF_3+BN=BF_2+FBN$



Reaction rate [cm^3 mol-1 s^-1]
10000/T [K^-1]
BF3 + BN = BF2 + FBN
k(T) = 1179.4 T^2.88 exp(-48898/RT)
κ(T)k(T) = 752.6 T^2.93 exp(-48676/RT)
Γ(T)k(T) = 153.5 T^3.11 exp(-86768/RT)



Reaction rate [cm^3 mol-1 s^-1]
10000/T [K^-1]
BF3 + BN = BF2 + FNB
k(T) = 3459.1 T^2.75 exp(-34871/RT)
κ(T)k(T) = 2913.0 T^2.77 exp(-34791/RT)
Γ(T)k(T) = 2844.9 T^2.77 exp(-10020/RT)

Conclusion

We have studied the gas-phase BF_3 + BN ® BF_2 + FBN and BF_3 + BN ® BF_2 + FNB 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.

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