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Theoretical determination of accurate rate constants: Application to the decomposition of a single-molecule precursor

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Abstract

The ring opening is proposed to be the initial step in the unimolecular decomposition of a single-molecule precursor bisazido (dimethylaminopropyl)gallium (BAZIGA) used in a CVD process of gallium nitride. An efficient Monte Carlo importance sampling technique is developed to estimate the canonical partition functions and absolute entropies therefrom by taking the internal rotor hindrance and all coupling arising from the external and internal rotational degrees of freedom into account. This allows the estimation of the free energy difference in the ring opening process of BAZIGA to be made.

Canonical flexible transition state theory is applied to the radical Ga–C bond homolysis in the unimolecular decomposition of BAZIGA. The limiting high-pressure rate constant is calculated using a simple model for the potential energy surface based on density functional calculations.
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Keywords: Gallium nitride; CVD; Single-molecule precursor; Flexible transition state theory; Rate constant

1. Introduction

The ternary, wide-band gap, group-13 nitride semiconductors of the type AlGaN and InGaN have been established as important materials for a broad variety of applications including optoelectronic devices, particularly for short-wavelength LEDs and laser diodes. Recently, bisazido(dimethylaminopropyl) gallium (BAZIGA), **1** (see Fig. 1), has been shown to be a very attractive single molecule precursor for the chemical vapor deposition (CVD) of gallium nitride [1].

The modeling of many chemical processes, including combustion, catalysis, polymerization, etc., requires a detailed knowledge of entropic changes occurring during the reaction.

Therefore, partition functions are needed to calculate various thermodynamic properties of a system. The entropic contributions to free energies can be quite substantial especially at elevated temperatures and when large molecules are involved. In CVD processes, these contributions can play an important role in the unimolecular decomposition of especially large precursor molecules at elevated temperatures. For the determination of gas-phase rate constants this can become as important as the accuracy of the calculated potential energy surface (PES). For molecules, where several hindered internal rotations are present, the usual harmonic oscillator, rigid-rotator approximation is no longer valid. A proper treatment should take both the internal rotor hindrance and all coupling arising from the external and internal rotational degrees of freedom into account.

Computational fluid dynamics (CFD) is widely used in modeling of the whole process of the gallium nitride deposition in a reactor [2], where, among other things, the rate constants for the elementary reactions should be supplied.

In our efforts to elucidate the mechanism and rate constants of a CVD process using this particular single-molecule precursor, it is argued [3] that the ring opening (going from **1** to **2**) is the most

probable initial step in the unimolecular decomposition of **1**. The whole decomposition process for BAZIGA can be represented by the following scheme:
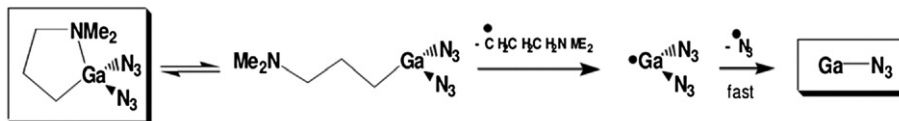
Previously [3] it has been shown that at temperatures relevant for the CVD process (1000 °C) the entropic contribution from the rotational degrees of freedom of the open arm of BAZIGA, **2**, obtained from a separable (uncoupled) treatment of the external and internal rotations differs from that based on the rigid rotor-harmonic oscillator approximation. Below we develop a fully coupled treatment of the rotational degrees of freedom for **2**. Next, we describe the application of the canonical flexible transition state theory (CFTST) to the radical Ga–C bond homolysis by treating transitional modes via efficient numerical integration. The configuration integral over the transitional modes is evaluated using a Monte Carlo technique with stratified sampling in the temperature range from 400 to 1000 K.

Whereas the rigid rotor-harmonic approximation seems quite reasonable for **1**, this is not the case for the open arm, **2**, due to the presence of multiple large amplitude internal rotations about single bonds. A fully coupled approach developed recently for a non-rigid chain molecule [4] is adopted here for the calculation of the rotational entropy for the open arm. This approach has been recently applied by us [3] for the estimation of rotational entropies for a number of small straight chain *n*-alkanes from ethane to octane. In the present work, we use the technique now for the first time for a much more complicated metal-organic CVD precursor. The approach is based on an efficient (importance sampling) Monte Carlo integration of the configurational phase space, thus accounting for all relevant rotamers.

to properly model the steric hindrance in the different configurations. The influence of the methodology to calculate the rotational partition function on the free energy difference between the closed (**1**) and the open (**2**) form of BAZIGA will be discussed.

2. Computational details

2.1. Ring opening in BAZIGA

2.1.1. Canonical partition function

Among the methods available for non-linear polyatomic molecules, a semiclassical approach developed long ago by Pitzer et al. [5,6] seems to be the most attractive one, especially when thermodynamic functions are required at elevated temperatures. The expression for the classical rotational partition function is well-known and is given by:

$$Q_{\text{rot}} = \frac{8\pi^2}{\sigma} \frac{(2\pi k_B T)^{(n+3)/2}}{h^{(n+3)}} \int_0^{2\pi} \dots \int_0^{2\pi} \sqrt{|A(\phi)|} e^{-\frac{V(\phi)}{k_B T}} d\phi, \quad (1)$$

where *n* is the number of internal rotational degrees of freedom, $|A|$ is the determinant of the generalized inertial tensor matrix (GIT); $V(\phi)$ is the hindering potential for the internal rotation; $\phi = (\phi_1, \phi_2, ..., \phi_n)$ is a vector of the
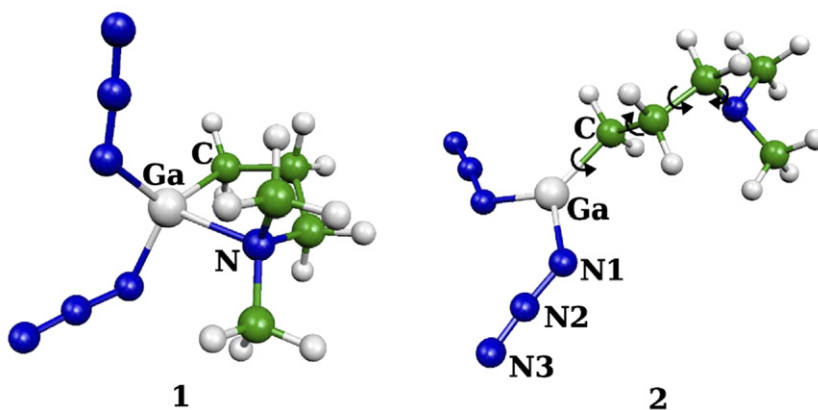

Fig. 1. Molecular structures for closed (**1**) and open (**2**) BAZIGA.

generalized internal coordinates describing the internal rotations; T is the absolute temperature (K); σ is the combined (internal and external) symmetry number, and k_B and h are Boltzmann's and Planck's constants.

Since the classical partition function is known to overestimate its quantum counterpart at low temperatures, a correction is needed to get reliable thermodynamic functions. The rotational partition function (Eq. (1)) can be approximately corrected for quantum mechanical effects at low temperatures with the help of a widely used method of Pitzer and Gwinn [5] by appending the factor

$$\frac{Q_{HO}(\text{quant})}{Q_{HO}(\text{class})} = \prod_{i=1}^{n} \frac{u_i}{\sinh(u_i)}, u_i = \frac{hc v_i}{2 k_B T}, \tag{2}$$

where $Q_{HO}(\text{quant})$ and $Q_{HO}(\text{class})$ are the quantum mechanical and classical harmonic oscillator partition functions, respectively; v_i are the harmonic vibrational frequencies corresponding to the torsional normal modes in cm^{-1} and c is the speed of light.

The rotational entropy of a gas-phase molecule can be determined from the standard thermodynamic formula:

$$S_{\text{rot}} = k_B \left(\ln Q_{\text{rot}} + T \frac{d \ln Q_{\text{rot}}}{dT} \right). \tag{3}$$

A general scheme to determine canonic partition functions (Eq. (1)) via a Monte Carlo phase-space multidimensional integration based on a molecular mechanics force field has recently been proposed [7]. We have improved upon this method by making use of a numerically much more efficient Monte Carlo importance sampling technique [4] and implemented it to be used with the TINKER program package [8]. It is based on the VEGAS importance sampling algorithm of Lepage [9]. We used a modified version of the subroutine taken from [10]. For more details and our implementation, see [4].

2.1.2. Force field parameterization

A great deal of effort has been, and still is devoted to the development of reliable force fields used in molecular mechanics and dynamics simulations of the properties of complex molecular systems, see, for example, [11,12]. For the present work, we use a simplified approach where the force parameters for a particular fragment are not optimized but instead taken directly from the DFT calculations performed at the B3LYP/cc-pVDZ level [13–15] with the Gaussian program package [16]. Molecular mechanics calculations utilized the TINKER software package [8] using the MM3(2000) force field [17] for the aliphatic carbon (atom type 1) and hydrogen (atom type 5) atoms and for the sp^3 nitrogen atom (atom type 8). This force field is supplemented with additional parameters for the gallium diazide fragment taken from DFT calculations carried out for **2** and for the two model systems, $(N_3)_2Ga-C_2H_5$ and $(N_3)_2Ga-C_3H_7$. Four new atomic types are introduced: Ga, N1(–Ga), N2(=N-) and N3(–N2), see Fig. 1 for the numbering. The van der Waals parameters for the Ga atom is taken from [18]. The available van der Waals parameters for the

central nitrogen atom in the azide group are used for all nitrogens in the group, although, as has been shown recently [19], these three nitrogens in aliphatic azides should be assigned slightly different values. No distinction is made between the two azide groups. The intramolecular force parameters (bond stretchings, angle bendings, etc.) are taken as the (unscaled) force constants calculated for the fully optimized structure of **2** at the B3LYP/cc-pVDZ level. The Hessian matrix in Cartesian coordinates was transformed to a set of force constants in (redundant) internal coordinates [20]. Four additional torsional energy terms are introduced. As with MM3, we use a six-term Fourier series expansion to represent torsional energy:

$$V(\phi) = \frac{1}{2} \sum_{n=1}^{6} V_i [1 + \cos(n\phi - \alpha_n)]. \tag{4}$$

The parameters V_1, V_2 and V_3 are obtained by fitting the corresponding one-dimensional torsional potentials calculated by the DFT for the model systems (about the Ga–C, Ga–N1 bonds in $(N_3)_2Ga-C_2H_5$ and about the (Ga)C–C(C) bond in $(N_3)_2Ga-C_3H_7$). One-dimensional torsional potentials were calculated by fixing the respective dihedral angle in the range of 0–360° with the step size of 30° and relaxing all the

Table 1
Parameter set for the gallium diazide fragment

Bond lengths and stretching parameters

Bond	Reference distance, Å	Force parameter, mdyn/Å
Ga–C1	1.97	2.3
Ga–N1	1.88	2.8
N1–N2	1.23	11.3
N2–N3	1.14	18.6

Angle bending

Atoms	Reference angle, °	Force parameter, mdyn Å/rad²
Ga–C–C	114.5	0.42
Ga–C–H	107.0	0.37
C–Ga–N1	125.0[a]	0.18
N1–Ga–N1	110.0	0.24
Ga–N1–N2	123.0	0.36
N1–N2–N3	180.0	0.74

Out-of-plane bending

(N1,N1)Ga–C		0.17

Torsional parameters, kcal/mol

Atom types	V_1	V_2	V_3
C–C–Ga–N1	0.103	0.365	0.027
C–Ga–N1–N2	0.345	2.719	0.294
Ga–C–C–C	0.358	−0.419	2.966
N1–Ga–N1–N2	−0.530	4.069	0.617

van der Waals' parameters

Atom	R_{vdw}, Å	ε, kcal/mol
Ga	2.46	0.2
N (azide)[b]	1.93	0.04

[a] Average value.
[b] Three nitrogen atoms in the azide group are assumed to have the same parameters.

remaining internal degrees of freedom. All off-diagonal terms representing coupling interactions between internal coordinates in the gallium diazide fragment are neglected. The additional force field parameters used in this work are given in Table 1.

Since we did not include any attractive terms in the force field describing the donor–acceptor Ga–N(Me$_2$) bond which lead to the stabilization of **1** compared to **2**, care should be taken to avoid sampling the region in the configurational space of **2** which in reality belongs to **1**. We exclude the (quite rare) trials with the short Ga–N(Me$_2$) distance (<2.3 Å) by our sampling technique from the MC summation.

2.2. CFTST of the Ga–C bond homolysis

For the location of the loose transition states during unimolecular decomposition of **2** into the Ga(N$_3$)$_2$ and dimethylaminopropyl radicals, we adopted the method developed by Klippenstein et al. [21]. The computer code VARIFLEX was used in our calculations of the rate constants [22].

A formula for the CFTST expression for the thermal reaction rate constant evaluates classically the contribution to the rate constant from transitional degrees of freedom (those that evolve from free rotations in the limit of infinite separation of the reactants). It contains the product of two factors: one that exclusively depends on the collision kinematics and one that exclusively depends on the potential energy surface that controls the transitional degrees of freedom. The high-pressure limiting canonical rate constant for the unimolecular decomposition reaction is given by [21b]:

$$k(T) = g_e \frac{k_B T}{h} \frac{\sigma}{\sigma^\#} \frac{Q_c^\#(T)Q_{pd}^\#(T)Q_{fr1}^\#(T)Q_{fr2}^\#(T)\Gamma^\#(T)}{Q_{react}(T)} e^{\frac{-V(R^\#)}{k_B T}},$$

(5)

where g_e is the ratio of electronic degeneracies for the transition state (TS) and separated radicals, $\sigma/\sigma^\#$ is the ratio of reactant and TS symmetry factors, $Q_{react}(T)$ is the total partition function for the reactant (**2**), $Q_c^\#(T)$ and $Q_{fr,i}^\#(T)$ are the vibrational (conserved) and rotational partition functions for the fragments at the TS, $Q_{pd}^\#(T) = 8\pi^2 \mu (R^\#)^2 k_B T/h^2$ (μ is the reduced mass of the two fragments) is a pseudo diatomic partition function for the relative orbital motion of fragments at the TS, $V(R)$ is the potential energy along the reaction coordinate and $\Gamma^\#(T)$ is the configuration integral.

We have separated the potential into three parts: (1) the potential along the reaction coordinate; (2) the potential corresponding to the "conserved" degrees of freedom; and (3) the potential for the "transitional" degrees of freedom which depends on the relative orientation angles of the fragments.

The potential along the reaction coordinate is represented by a Varshni potential [23]:

$$V(R) = D_e \left(1 - \frac{R_0}{R} e^{-\beta\left(R^2 - R_0^2\right)}\right)^2 - D_e,$$

(6)

where D_e is the "classical" bond energy (i.e., not including zero-point vibrational energies), R the reaction coordinate, and R_0 its equilibrium value. In the present case, the reaction coordinate is

the distance between the two bonding atoms (Ga and C). The parameters for the Varshni function (D_e and β) were obtained by density functional theory (B3LYP/cc-pVDZ) from a number of fully relaxed calculations with the fixed Ga–C separation (up to 5 Å).

The potential for the conserved coordinates is assumed to be harmonic. This potential corresponds to the degrees of freedom that can be identified as normal-mode vibrations in the separated fragments. The transition states for bond fission reactions normally lie so far out in the asymptotic region of the PES that it is reasonable to assume that these degrees of freedom, and their corresponding frequencies, maintain their integrity in going from the separated fragments to the transition states. Thus, the fragment geometries and their vibrational frequencies were assumed to be the same in the transition state.

The potential for the transitional coordinates are represented in terms of five internal angles: the N–Ga–C and Ga–C–C bond angles, two torsional angles: N–Ga–C–C and Ga–C–C–H and one out-of-plane N–Ga(N)–C wagging angle. The potential is expressed as a sum of products (in pairs) of sinusoidal functions (see Eq. (4) of Ref. [24]). The coefficients in the expression are functions of the bond distance R and are determined by calculating the appropriate force constant matrix in terms of these five internal angles using DFT at the potential minimum, $F_{ij}(R_0)$, and assuming that these matrix elements decay exponentially with bond distance:

$$F_{ij}(R) = F_{ij}(R_0)e^{-\eta_k(R-R_0)},$$

(7)

where η_k ($k=1,2,..,5$) are some adjustable parameters for the five chosen internal angles which were set to around 1.0 Å^{-1}. Anisotropy of the stretching potential (see Eq. (6) above) was also taken into account by multiplying it with the squared cosine functions the arguments of which are the deviations from the bond angles (see above) at the potential minimum.

We have locally modified the Monte Carlo integration routine to allow for the stratification in all 5 dimensions. In the presented calculations the range of each angle was divided into 15 strata and the relative error of the Monte Carlo integration was 0.1%.

3. Results and discussion

3.1. Ring opening in BAZIGA

The force field described above in combination with the importance sampling MC integration strategy outlined in our previous paper [4] were used to calculate the rotational part of the canonical partition function of **2** (Eq. (1)). The dimensionality of the integral is 8 (all rotatable bonds are shown in Fig. 1). The rotational partition function was then corrected for quantum effects at low temperatures by the Pitzer–Gwinn method [5] using 8 torsional frequencies for the lowest energy conformer found by a simple stochastic conformational search described in [4]. The symmetry number (σ) is set to 1 and a threefold symmetry of the torsional potential for the two methyl groups is

Table 2
Comparison of entropic contributions of 8 internal rotations and free energy differences for the ring opening process in BAZIGA

T, K	S, cal/mol/K[a]		
	Coupled[b]	Uncoupled[b]	Harmonic oscillator
298.16	73.2	75.2	64.7
500	84.8	86.4	74.2
700	91.8	93.2	80.5
900	96.7	98.3	85.2
1100	100.3	101.6	89.0
	$\triangle G$, kcal/mol[c]		
500	11.44	10.56	13.39
700	8.49	7.52	12.29
900	5.61	4.54	10.7
1100	2.66	1.36	8.03

[a] Translational entropy is not included.
[b] Pitzer–Gwinn corrections are not included.
[c] ZPE is included (B3LYP/cc-pVDZ).

taken into account. The values for the rotational entropy of **2** are taken as an average over 10 runs. Each run was terminated when a desired accuracy (1% relative error in the integral of Eq. (1)) has been achieved. The Pitzer–Gwinn correction for quantum effects at low temperatures adds to the entropy of **2** the value of 0.3 cal/mol/K at room temperature being negligible at high temperatures, as expected.

The vibrational part of the entropy is calculated by the standard thermodynamic formula using the harmonic oscillator approximation. The vibrational frequencies correspond to the lowest energy conformation optimized with the present force field. With the present force field, the values of low frequencies which correspond mainly (they are coupled to other modes) to 8 torsional vibrations are (in cm^{-1}): 6.9, 35.2, 71.1 (Ga–N (azide), syn), 82.4, 98.6, 129.7 (Ga–N(azide), anti), 256.1 (Me, syn) and 282.8 (Me, anti). These are favorably compared to those obtained previously by our DFT calculations (B3LYP/cc-pVDZ) for **2**: 10.7, 27.2, 60.7, 70.1 (Ga–N(azide), syn), 86.5 (Ga–N(azide), anti), 121.4, 232.5 (Me, syn) and 247.8 (Me, anti). Moreover, when two lowest energy structures obtained from DFT and from the present force field are compared, the overall vibrational part of the entropy (69 frequencies, harmonic approximation) is reproduced within 0.2 cal/mol/K by the simplified force field employed here. The entropies at various temperatures are compared in Table 2 along with the values based on an uncoupled approach.

For the uncoupled case, a number of one-dimensional importance sampling MC integrations are performed and the rotational entropies are obtained for **2** as averages over 10 runs. The reduced moments of inertia were calculated by projecting the instantaneous three principal moments of inertia out from the 4×4 GIT matrix, thus fully accounting for the coupling of each internal rotational degree of freedom with the overall rotation while ignoring all kinetic couplings between internal rotations. In this approach, the reduced moments of inertia were allowed to vary with the corresponding dihedral angle. Effective one-dimensional torsional potentials were optimized based on the present force field with the corresponding dihedral angle

fixed at a randomly generated value. The entropic contribution from the overall rotation for the lowest energy conformer is then added to the sum of the uncoupled one-dimensional rotational entropies. Also listed in Table 2 are the entropic contributions calculated with the harmonic approximation using 8 frequencies which correspond to the torsional modes of **2**.

Our results suggest, that, the harmonic oscillator approximation heavily underestimates the entropic contributions of 8 internal rotations of the open arm due to a much more restricted phase space available for the molecule, as expected. On the other hand, the uncoupled treatment of 8 internal degrees of freedom gives overestimated values as compared to the coupled approach (see Table 2).

In our recent work [3], we have applied an uncoupled approach in combination with the effective one-dimensional torsion potentials calculated at the B3LYP/cc-pVDZ level to estimate the entropic contributions of 4 internal rotational degrees of freedom of **2** which contribute significantly to the overall entropy change in the arm opening process (rotatable bonds are shown in Fig. 1). The uncoupled data from our combined DFT/MM force field simulations are in good agreement with the uncoupled results obtained previously utilizing pure DFT calculations [3] with the difference being 2 to 3 times smaller than the difference between the coupled and uncoupled DFT/MM results (see Table 2). Since the entropic contributions from both the two methyl torsions and the two torsions around Ga–N(azide) bonds are to a good approximation similar in **1** and **2**, they will nearly cancel in the free energy difference calculation of the arm opening process (see Fig. 1). In Table 2, free energy differences are compared based on three different treatments for these 4 torsional modes in **2**. Using these data, one can estimate the error in a typical unimolecular rate constant that results from treating these 4 rotations as vibrations by using the following simplified equation for the rate constant:

$$k(T) = \frac{k_B T}{h} e^{-\frac{\triangle G^{\#}}{k_B T}}. \tag{8}$$

We can anticipate that in this temperature range a transition state on the free energy surface for the ring opening process occurs closer to **2** than to **1**. Hence, assuming that the free energy of activation, $\Delta G^{\#}$, can be approximated by the values from Table 2, the rate constant at 1100 K is calculated to be an order of magnitude smaller when the usual harmonic approximation is used (last column) compared to the value based on the coupled hindered rotor treatment. The free energy difference calculated within the harmonic approximation at 1100 K overestimates by 5.4 kcal/mol the value based on the coupled

Table 3
Rate constants for the Ga–C bond homolysis of **2**

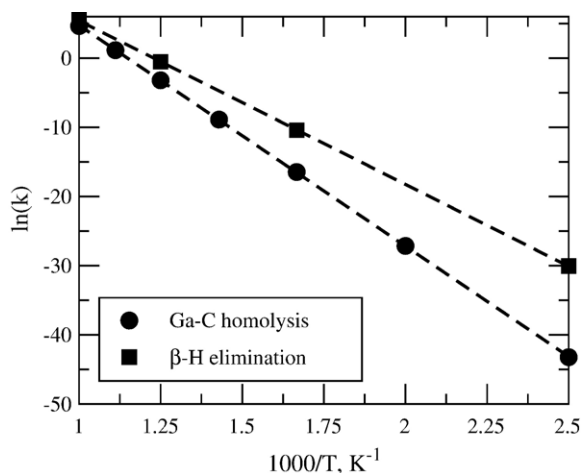| T, K	$R^{\#}$, Å	k, s^{-1}
400	4.6	1.68×10^{-19}
600	4.5	7.13×10^{-8}
800	4.3	4.05×10^{-2}
1000	4.2	103.7

Fig. 2. Arrhenius plot for the Ga–C bond homolysis and β-H elimination of **2**. Dashed lines through the calculated points are the least-squares fit to the Arrhenius equation.

approach, which amounts to ca. 30% of the corresponding enthalpy increase of 18.5 kcal/mol (B3LYP/cc-pVDZ, corrected for ZPE) caused by the breaking of the Ga–N bond. We conclude that the standard harmonic oscillator approximation is a very crude one for the case studied, producing an unreliable estimate of the free energy difference as compared to the accepted "chemical accuracy" of 2 kcal/mol.

3.2. CFTST of the Ga–C bond homolysis

In Table 3 are listed the calculated values of rate constants for the Ga–C bond homolysis of **2** and the corresponding locations of transition state at different temperatures.

For the temperature range from 400 to 1000 K, the calculated rate constants can be fitted by the effective Arrhenius rate law with a preexponential factor $A = 1.0 \times 10^{16}$ s^{-1} and an apparent activation energy of $E_a = 63$ kcal/mol (see Fig. 2).

The influence of the flexibility of the dimethylaminopropyl radical (internal rotations) on the rate constant can be accounted for by considering its stable conformations and evaluating the rate constant for each of them. To this end, we performed PES scan for this radical (at the B3LYP/cc-pVDZ level of theory) and found 5 geometrical arrangements corresponding to local minima. As can be seen from Eq. (5), different conformers should contribute mainly through the terms $Q_{fr}^{\#}(T)$ (via the product of their three inertial moments of the dimethylaminopropyl radical) and $Q_{pd}^{\#}(T)$ (via averaged center-of-mass separation) at a given temperature. We found that the rate constant increases by just a factor of 2 when going to a conformer with the largest product of the inertial moments.

Our values for the Arrhenius parameters can be compared with those calculated previously for the Ga–C bond homolysis in some gallium alkyl compounds: $Ga(CH_3)_3$, $Ga(C_2H_5)_3$ and $Ga(C_4H_9)_3$. Boero et al. [25], in their first principles molecular dynamics study, have estimated the activation energy to be 60.9, 60.2 and 60.1 kcal/mol for $Ga(CH_3)_3$, $Ga(C_2H_5)_3$ and $Ga(C_4H_9)_3$, respectively, with the Ga–C distance of ca. 4.3 Å at the TS ($T = 550$ K). For the decomposition of the $Ga(CH_3)_3$, Cardelino

et al. [26] predicted the values of 2.0×10^{20} s^{-1} and 64 kcal/mol for the preexponential factor and activation energy, respectively. In our recent study on the first Ga–C bond homolysis of $Ga(CH_3)_3$, we have reported the values of 3.13×10^{16} s^{-1} and 75.6 kcal/mol for the preexponential factor and activation energy [27].

We also note that, according to our calculations (tight-binding transition state; B3LYP/cc-pVDZ), the β-H elimination channel for the open arm of BAZIGA is a competing reaction due to its activation barrier (46 kcal/mol) significantly lower than a direct Ga–C bond homolysis. However, as can be seen from Fig. 2, at elevated temperatures (>1000 K), the fragmentation channel will be preferred due to the larger entropic contribution as compared to the β-H elimination.

4. Conclusions

We presented a very promising approach to reliably estimate the entropic contribution to the free energy needed in the modeling of various chemical processes involving complex non-rigid molecular systems. To be of practical use, the method should be able to reproduce accurately the important features on the potential energy surface (stationary points and rotational barriers) as well as local curvatures at the minima. It is shown that at temperatures relevant for the CVD process the entropic contributions from the rotational degrees of freedom of the open arm of BAZIGA differ both from those calculated by a separable (uncoupled) treatment of the external and internal rotations and from those based on the rigid rotor-harmonic oscillator approximation.

The CFTST approach can be successfully used to evaluate the rate constants for the unimolecular decomposition of such a complex system like BAZIGA.

Acknowledgements

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