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Influence of the Molecular Environment on the Three-Center versus Four-Center Elimination of HBr from Vinyl Bromide: A Theoretical Approach

Sándor Kunsági-Máté,*,† Eszter Végh,† Géza Nagy,†,‡ and László Kollár‡,§

Department of General and Physical Chemistry, University of Pécs, H-7624 Pécs, Hungary,
Department of Inorganic Chemistry, University of Pécs, H-7624 Pécs, Hungary, and Research Group for
Chemical Sensors of the Hungarian Academy of Sciences, H-7624 Pécs, Hungary

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The dynamics of dissociative reactions of vinyl bromide was investigated by Langevin molecular dynamics method in the absence and in the presence of frictional interaction between the molecule and its environment. The results show a redistribution of the vibrational energy on the bonds of vinyl bromide under the effect of frictional interaction. This redistribution can modify the reaction rates of vinyl bromide dissociation channels. Increasing the frictional coupling between vinyl bromide and its environment, the vibrational energy redistribution increases the transition probability on the four-center HBr elimination channel. This environment-induced change on the rate of reaction pathways demonstrates that the existence of friction may not guarantee statistical behavior of the dissociation processes of vinyl bromide.

Introduction

The dissociation reactions of halogenated ethylene (vinyl halides, CH_2CHX, X = F, Cl, or Br) have provided a fruitful testing ground for unimolecular reaction theories. Therefore, they were investigated seriously by both experimental[1−5] and theoretical[6−10] studies in past decades. A detailed mechanism of dissociation proceeds via multiple channels.[11] The dissociation mechanism strongly depends on the identity of the halogen substitution, which influences the energetics of dissociation pathways, i.e., the relative sites of transition states on which the system undergoes the fragmentation processes. The recent studies of these molecules are particularly interesting because their reaction dynamics induced by photoexcitation can be experimentally investigated by measuring the vibration energy distribution of the dissociated products.[12−16]

In a quite early work, Johnson and Price reported[17] that during the dissociation of photolyzed vinyl bromide after the excitation by Xe flash lamp the HBr formation is the observed major channel. Another study has indicated that the photodissociation channels are dominated by both Br and HBr elimination.[18] The Br dissociation is suggested as a result of the C−Br bond rupture in an electronically excited state of vinyl bromide.[19] The HBr elimination could proceed in a variety of ways when the vinyl bromide is initially excited to a number of closely spaced repulsive potential energy surfaces.[20] In the excited electronic state of vinyl bromide, direct elimination of the HBr molecule from the barrierless repulsive surface could also occur similarly to the simple Br elimination.[18] It is also possible that initial excitation is followed by internal conversions to the ground electronic state. This process leaves the vinyl bromide molecule in a significantly high excess vibrational energy condition. Recent theoretical[21] and experimental[16] findings show that this internal conversion will occur with high efficiency because the molecular elimination of HBr involves the breaking of two bonds (CBr and one of the CH bonds), so excess vibrational energy is required for these elimination channels.[19] After these internal conversions, there are two energetically favored pathways for HBr elimination on the ground electronic energy surface. The dissociation of HBr from vinyl bromide results in a C_2H_2 product in two different forms: vinylidene and acetylene. In the first case, when vinylidene is formed as a product, HBr elimination involves the breaking of CBr and CH bonds joined to the same C atom of the vinyl bromide molecule. Therefore, three atoms take part in this dissociation process, and it is called a three-centered HBr elimination. Otherwise, when acetylene is formed after HBr elimination, the breaking of CBr and CH (cis to Br) bonds joined to the different C atoms of the vinyl bromide molecule occurs, and in this case, four atoms play a role in the HBr elimination. This process is known as four-centered elimination. Going back to the first, three-centered pathway, vinylidene as a final reaction product was not found experimentally. This can be explained by the low energy barrier along the vinylidene to acetylene isomerization coordinate (≈2.6 kcal/mol[22−24]). This means that the vinylidene product quickly isomerizes to the energetically more stable acetylene.[25] Finally, both three-centered and four-centered eliminations of HBr eventually result in the same set of products, which makes it difficult to determine the favored dissociation channel from product identification alone. However, the three- and four-centered mechanisms will give distinctly different product energy distributions. This enables the identification of the products by measuring their IR emission.[26,27] Recently this property of photofragmentation processes of vinyl halides is extensively used for the identification of reaction channels.[16,28]

When the reports about dissociation of vinyl bromide are overviewed, different results on three-center versus four-center elimination of the HBr molecule can be found. For a detailed examination of energetically open reaction channels, the potential energy hypersurface of the dissociative reactions of vinyl bromide was determined recently by high-level ab initio method.[21] The analytic form of the hypersurface was developed primarily by least-squares fitting of appropriately chosen

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* To whom correspondence should be addressed.

† Department of General and Physical Chemistry, University of Pécs.

‡ Research Group for Chemical Sensors of the Hungarian Academy of Sciences.

§ Department of Inorganic Chemistry, University of Pécs.

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TABLE 1: Selected Energetically Favored Reaction Channels of Dissociative HBr Elimination from Vinyl Bromide that Are Examined in This Work

channel label	reaction	description	transition state label
I.	$C_2H_3Br \rightarrow HBr + H_2C{=}C$: (vinylidene)	three-center elimination	TS3
Ia.	$H_2C{=}C$: (vinylidene) $\rightarrow HC{\equiv}CH$ (acetylene)	isomerization	TSva
II.	$C_2H_3Br \rightarrow HBr + HC{\equiv}CH$ (acetylene)	four-center elimination	TS4

functional forms to the results of ab initio electronic structure calculations. The reaction dynamics of vibrationally excited vinyl bromide have been investigated using the classical trajectory method[29,30] on a global, analytic potential energy hypersurface. It was concluded that vibration energy distribution of HBr formed from vinyl bromide via a three-center elimination reaction is Boltzmann, and the characteristic temperature of the HBr product formed was found to be 7084 K.[21] These results are in agreement with the experimentally determined vibrational energy distribution,[28] and in both papers, it is assumed that HBr is formed almost solely via a three-center elimination mechanism because this channel has a lower transition state energy than that of the four-centered elimination. However, Wodtke et al. employed the time-of-flight method to measure distributions of translational energy and anisotropy parameters of photodissociation products Br and HBr and reported a branching ratio of 1.28 between these two channels.[31] Saito et al. employed a shock tube to investigate the formation of HBr via thermal decomposition of vinyl bromide at 1300−2000 K, and they determined 230kJ/mol as the barrier.[32] This value is much smaller than theoretically predicted barriers of 308 and 340 kJ/mol for three-center and four-center elimination, respectively.[10] Other experiments on photolysis of vinyl bromide in a Kr matrix also show quite a different branching ratio between three-center versus four-center elimination.[33,34] Recently, Liu et al. found agreement between experimental and theoretical energy distributions of dissociation products for three-center eliminations in an Ar matrix. However, the HBr vibrational distribution for the four-centered calculated mechanisms has not been found.[28]

The differences among the values obtained for the dissociation barriers makes probable that there are other effects affecting the fragmentation processes of vinyl bromide. Recently, Rahaman and Raff published an excellent work[35] regarding the time-dependent vibrational energy redistribution inside vinyl bromide at a highly excited vibrational state. The consequence of this redistribution being in accordance with the Rice−Ramsperger−Kassel−Marcus (RRKM) theory[36] is that it could make force on the reaction pathways for dissociation reactions of vinyl bromide.

In this paper, as another possible situation, we examine the influence of the molecular environment on the vibrational energy redistribution in vinyl bromide by modeling the effect of collisions and the effect of dissipative energy change between vinyl bromide and its environment. We calculate the transition state energies for three- and four-center eliminations, the conformations in these states, as well as the vibration frequencies of the molecule and compare them with the regarded results. As the most important data, the vibrational energy redistribution under the effect of environmental molecules will be discussed. Finally, mechanistic details of a reaction pathway based on the calculation of the redistributed vibrational energy will be presented.

Method

The quantum chemical calculations described here were carried out using the AM1 (Austin Model) method[37] implemented in the program HyperChem Professional 5.1.[38] Recently this method has been used to study the electronic properties of interacted species,[39] thermochemistry,[40] and energetics of chemical reactions[41−44] also in structure−activity relationship analysis[45] where the system contains a vinyl segment. Especially, this method has been chosen to study the three-center versus four-center dissociation of vinyl fluoride.[46] Polak-Ribiere and quadratic linear synchronous transit search were used for geometry optimizations and transition state calculations,[47,48] respectively. The transition state search was done in both forward and reverse directions. For dynamics calculations, the Langevin approach[49−51] was used with HyperChem package.[38] Langevin dynamics simulates the effect of molecular collisions and the resulting dissipation of energy that occurs in real experimental conditions without explicitly including the surrounding molecules. This is accomplished by adding a random force (to model the effect of collisions) and a frictional force (to model dissipative losses) to each atom at each time step during the simulation. Mathematically, this is expressed by the Langevin equation of motion:

$$m_i a_i = F_i - \gamma m_i v_i + R_i \tag{1}$$

Here, γ is the friction coefficient of the buffer, in units of ps^{-1} and R_i is the random force imparted to the atoms of examined molecule by the environment. The friction coefficient is related to the diffusion constant D of the buffer by Einstein's relation:

$$\gamma = \frac{k_B T}{m_i D} \tag{2}$$

The random force is calculated as a random number, taken from a Gaussian distribution, with an average value of zero. We used this method to examine the effect of the molecular environment of vinyl bromide during its dissociative reaction by scaling the frictional coefficient from $\gamma = 0$ (pure collisional interaction) to 1 (collisional interaction with partial dissipative energy losses). Using the experimental diffusion data of Ar,[52] which is the frequently used bath gas in regarded experiments, $\gamma = 0.11$ can be estimate at standard contidions. The diffusion coefficient is inversely proportional to pressure as long as the gas is in a region where binary collisions dominate. Because the pressure of the bath gas is usually varied from zero to a few hundreds kPa in the experiments (e.g., ref 55), a wider range of the frictional coefficients was investigated in this work.

Results

Static Reaction Map. Table 1 shows the two energetically favored fragmentation processes of vinyl bromide. Using the semiempirical AM1 method described above, first we determined the optimized geometries of the molecules considered to take part in these processes. The calculated energies of reactants and products as well as that of the transition states are shown in Figure 1. The energy values were calculated in relative to the total energy of relaxed vinyl bromide. Relevant geometry parameters of the system in transition states TS3 and TS4 are shown in Figure 2 and are summarized in Table 2. The ground-state geometry of vinyl bromide calculated with the AM1 method using the Polak-Ribiere algorithm was compared with other theoretical[21] and experimental[57] results in Table 3.

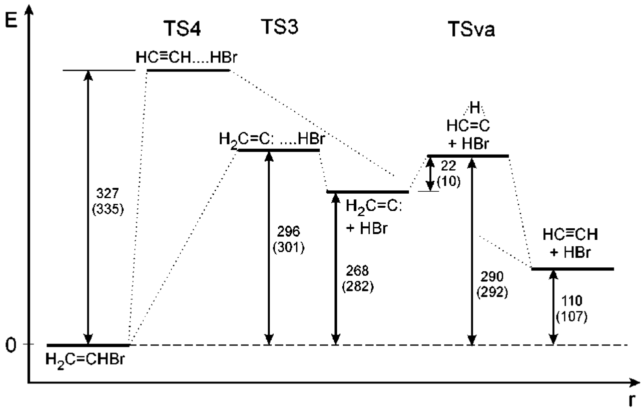

Figure 1. Energy diagram for the three-center and four-center elimination processes of HBr from vinyl bromide. The numbers are the AM1 energies in kJ/mol. The corresponding MP4 results[10] are given in parentheses.

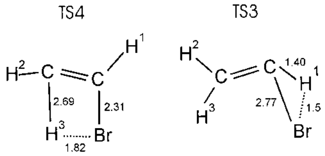

Figure 2. Geometries of transition states for four-center elimination (TS4) and three-center elimination (TS3) of HBr from vinyl bromide predicted with the AM1 synchronous transit calculation.

TABLE 2: Predicted AM1 Geometry of Transition States of Vinyl Bromide during Four Centered (TS4) and Three Centered (TS3) HBr Elimination Channels[a]

variable	TS4	TS3
	Bond Lengths	
C═C	1.2915	1.2983
C−Br	2.3191	2.7729
$C-H^1$	1.0975	1.4028
$C-H^2$	1.0629	1.1068
$C-H^3$	2.6907	1.1018
	Angles	
$C-C-H^1$	125.28	218.82
C−C−Br	122.05	119.15
$C-C-H^2$	161.86	120.32
$Br-C-H^1$	112.67	22.03
H^2-C-H^3	89.78	112.92
	Dihedral Angles	
$H^2-C-C-H^1$	179.61	179.59
$H^3-C-C-H^1$	172.93	0.48
$H^2-C-C-Br$	0.020	179.84
$H^3-C-C-Br$	6.664	0.23

[a] For the geometries of the transition states, see Figure 2. Bond lengths are given in angstroms. Angles are given in degrees.

The sum of the total energy of the products (acetylene + HBr) is higher than the total energy of the reactant vinyl bromide which shows the endotherm character of the reaction. The difference between the total energies of reactants and products was found to be 110 kJ/mol in correspondence with the value of 107 kJ/mol determined at the ab initio level using MP4 (Møller−Plessett) perturbation corrections.[10] The barriers for three-center and four-center elimination were found to be 296 and 327 kJ/mol, respectively. These values are in agreement with the MP4 results (301 and 335 kJ/mol, respectively[10]). The vinylidene → acetylene interconversion occurs across a barrier of 22 kJ/mol which is higher than that of the reported theoretical value (10 kJ/mol[16]). The energy of the vinylidene + HBr system at the local stationary midpoint lies at 58 kJ/mol a level above the energy of the final acetylene + HBr products.

TABLE 3: Comparison of Predicted Vinyl Bromide Equilibrium Geometries for Bond Lengths, Angles, and Dihedral Angles with Another Theoretical Work and with the Experimental Data[a]

variable	this work	PES1[21]	expt[57]
	Bond Lengths		
C═C	1.328	1.3226	1.330
C−Br	1.859	1.8943	1.890
$C-H^1$	1.098	1.0706	1.077
$C-H^2$	1.100	1.0771	1.083
$C-H^3$	1.098	1.0686	1.085
	Angles		
$C-C-H^1$	122.6	123.59	124.2
C−C−Br	125.1	123.76	122.5
$C-C-H^2$	121.3	119.52	118.7
$Br-C-H^1$	112.2	112.65	113.3
H^2-C-H^3	114.9	118.21	120.0
	Dihedral Angles		
$H^2-C-C-H^1$	0.000	0.000	0.000
$H^3-C-C-H^1$	180.0	180.0	180.0
$H^2-C-C-Br$	180.0	180.0	180.0
$H^3-C-C-Br$	0.000	0.000	0.000

[a] Bond lengths are given in angstroms. Angles are given in degrees.

TABLE 4: Fundamental Vibrational Frequencies of Vinyl Bromide Calculated by the AM1 Method, Their Descriptions, Regarded Theoretical Values, and the Measured Values of These Frequencies

		fundamental vibrational wavenumbers (cm^{-1})		
mode	description	this work	PES1[21]	expt[53,54]
ν_1	C═C−Br bend	344	335	344
ν_2	CHBr wag	558	581	583
ν_3	C−Br stretch	624	593	613
ν_4	CH_2 wag	940	986	902
ν_5	$H_2C=CHBr$ torsion	1019	1053	942
ν_6	C═C−H bend (H cis to Br)	1064	1130	1006
ν_7	C═C−H bend (H trans to Br)	1220	1142	1256
ν_8	H−C−H bend	1398	1375	1373
ν_9	C═C stretch	1810	1765	1604
ν_{10}	C−H stretch	3151	3386	3027
ν_{11}	C−H stretch	3172	3478	3086
ν_{12}	C−H stretch	3205	3520	3113

Table 4. summarizes the results of theoretical analysis on vibrational normalmodes of vinyl bromide in comparison with other theoretical[35] and experimental[53,54] data. The description of the fundamental vibrations is given in the table.

Vibration Dynamics in the Ground Electronic State at 300 K. Effect of Collision with Environmental Molecules. To obtain the possible effect of collisions of vinyl bromide with molecules presented in the molecular environment, Langevin dynamics calculations were done. The temperature was set to 300 K. The frictional coefficient γ was set to zero, which means that the molecule−environment interactions are considered as purely kinetic only. The processes were examined in three different situations by varying the bath relaxation time value. The bath relaxation time, which characterizes the number of collisions, is given in picosecond per collisions unit, and it was set to 10, 1, and 0.1 fs during the simulation. The simulation time step was 0.1 fs, and 10 000 points were calculated in each run. In order to find an appropriate initial condition for Langevin dynamics, a "heating" algorithm implemented in HyperChem was used. This procedure heats the molecular system smoothly from lower temperatures to the temperature T at which it is desired to perform the molecular dynamics simulation. The starting geometry for this heating phase is a static initial structure. We used the optimized AM1 geometry of vinyl bromide as an initial structure, and the temperature step and

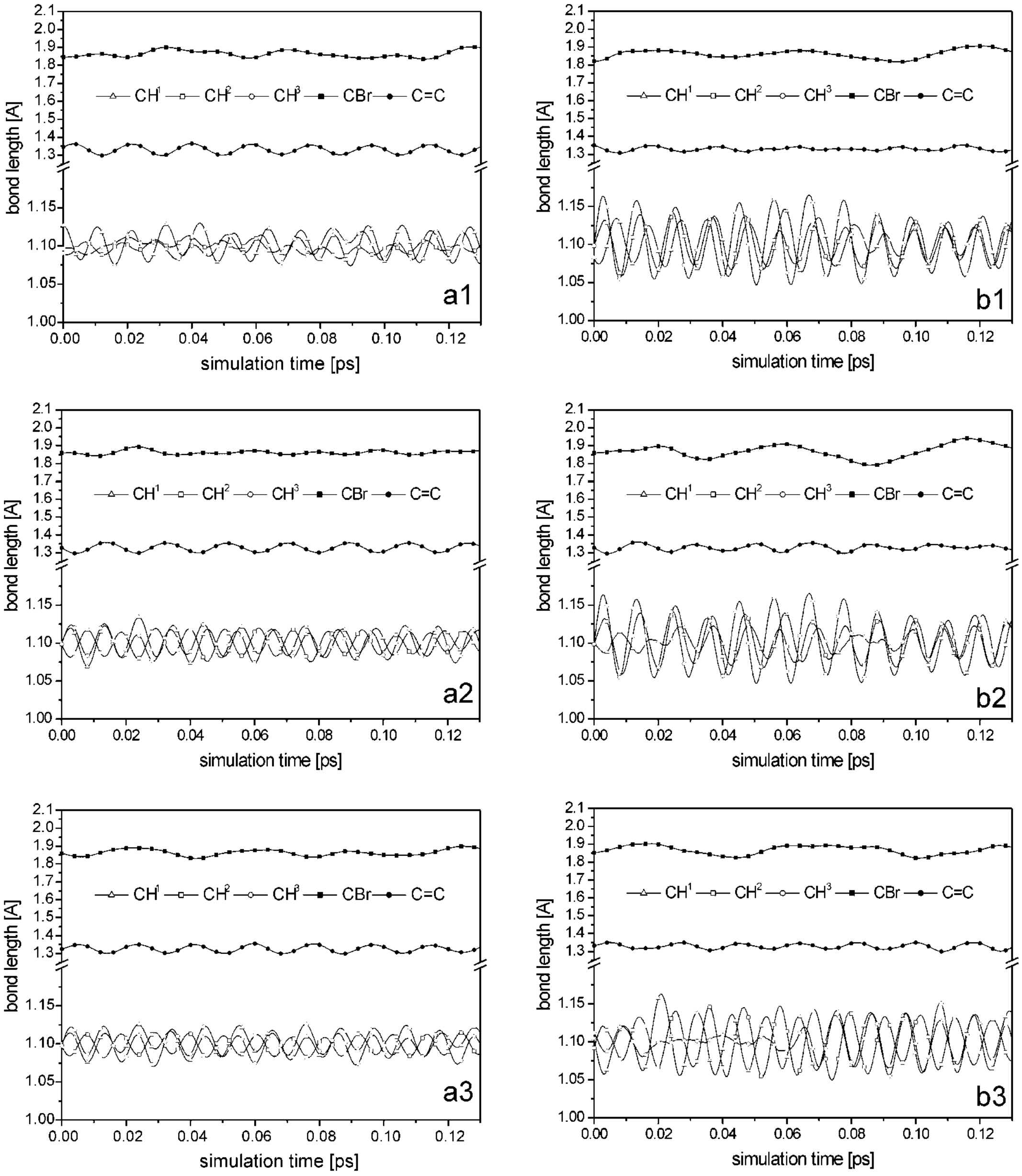

Figure 3. Variation of bond lengths of vinyl bromide molecule during Langevin dynamic calculation in absence (a series) and presence (b series) of the frictional interaction between the molecule and its environment. From up to down: bath relaxation time was setted 10, 1, and 0.1 fs, respectively. The average bond length was not changed; however, the amplitudes of the C−H vibrations increased significantly by the friction (b series).

the time step in the heating phase were set to 2 K and 0.1 fs, respectively.

These results are summarized in Figure 3 parts a1−a3. Parts a1−a3 of Figure 3 correspond to the bath relaxation time parameter of 10, 1, and 0.1 fs, respectively. This figure shows that by increasing the numbers of collisions between the vinyl bromide molecule and its environment no significant changes on the average bond lengths were found, whereas the amplitudes of bond stretching decreased in the case of a 0.1 fs bath relaxation time. At the same time, the fluctuation of the molecular energy also was examined. This was described as the standard deviation of molecular energy from the average value at the calculated 10 000 points. Table 5 summarizes the results and shows that the energy fluctuation decreases very fast with decreasing bath relaxation time.

As a consequence, the vibrational energy distribution of vinyl bromide could not be affected by the environment significantly if the interaction is purely kinetic.

Frictional Interaction of Vinyl Bromide with Its Environment. The effect of the friction of the vibrational energy distribution on the vinyl bromide molecule was examined by using the Langevin model with the variation of the frictional parameter γ in eq 1. Parts b1−b3 in Figure 3 show the variation of bond lengths of vinyl bromide as a function of the simulation time with the friction coefficient value of $\gamma = 1$. The bath relaxation times were chosen to be the same as those above, i.e., 10, 1, and 0.1 fs in cases b1, b2, and b3, respectively. It can be seen clearly that the most significant change occurs in the amplitudes of the CH bonds of the vinyl bromide molecule. The amplitudes detected for CH bond lengths are approximately five times higher in the presence of the friction (Figure 3, series

TABLE 5: Fluctuation of the Molecular Energy of Vinyl Bromide during a 1 ps Simulation Period in Dependence of Bath Relaxation Time

bath relaxation time [ps]	fluctuation [%]
0.01	9.2
0.001	1.8
0.0001	0.2

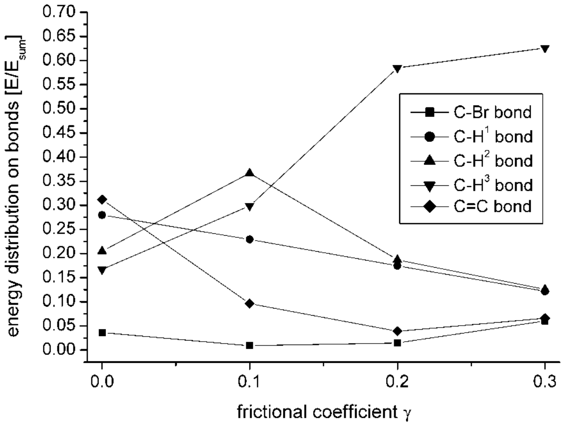

Figure 4. Vibrational energy distribution on the bonds of vinyl bromide in the dependence of frictional coefficient γ.

b) than that of the case when the molecule−environment interactions are purely kinetic (Figure 3, series a). As a consequence, the effect of friction manifests itself as a shift in the vibrational energy distribution on the bonds.

Dependence of the Vibrational Energy Distribution on the Frictional Parameter γ. The qualitative analysis of the distribution of the vibrational energy localized on the bonds of vinyl bromide was described as follows. After an equilibration at the given temperature, the Langevin simulations were run in 1 ps time intervals with a resolution of 0.1 fs. The lengths of all bonds of vinyl bromide were collected. The average amplitude of vibration was derived as the standard deviation of the regarded bond stretching data points from the average bond lengths. Using these amplitudes and the appropriate bond stretching frequencies (Table 4), the vibrational energy localized on a given bond was estimated by the definition of an oscillator. The total vibration energy was normalized to unity.

To obtain the dependence of the vibrational energy distribution on the frictional parameter γ, four Langevin simulation runs were performed. The temperature and bath relaxation time were set to 300 K and 1 fs, respectively. The frictional parameter γ was scaled from 0 to 0.3 by a step of 0.1. Figure 4. summarizes the results. The figure shows that the effect of friction on the atoms of vinyl bromide molecules manifests in a redistribution of the vibrational energy on the bonds. It also can be seen that the vibrational energy concentrates on the CH^3 bond when γ was set to 0.3. This is because the friction between the vinyl bromide molecule and its environment brings an external coupling into the normal mode vibrations of the molecule which can manifest as an antisotropic distribution of kinetic energy. By our opinion, this bears a relation to the asymmetry of the molecule. To support this idea, we have done the similar calculations for ethylene, where no similar effect were observed.

Temperature Dependence of the Vibrational Energy Distribution in Vinyl Bromide. During the pyrolysis of vinyl halides, the temperature range of 400−2000 K is usually used in shock tube measurements.[55] Therefore, further investigations on temperature effect on the energy distribution were necessary to compare the theoretical and experimental data. To do this, several sets of Langevin simulations were run where the temperature was scaled from 400 to 2000 K by 200 K steps.

Figure 5 shows the temperature dependence of the vibrational energy distribution in vinyl bromide calculated in the presence of friction ($\gamma = 0.3$). The result shows that the vibrational energies are shifted to the CH^3 bond stretching of the molecule and this shifted energy distribution is nearly unaffected by the temperature.

Friction-Controlled Four-Center Elimination of HBr from Vinyl Bromide. As we showed above, the frictional interaction of the vinyl bromide molecule with its environment results in the redistribution of the vibrational energy on the bonds of the molecule. The molecular dynamic simulation with the value of $\gamma = 0.3$ shows a shift of the vibrational energy onto the CH^3 bond of the molecule. The frictional interaction keeps the molecule in this shifted vibrational energy condition in a wide temperature range.

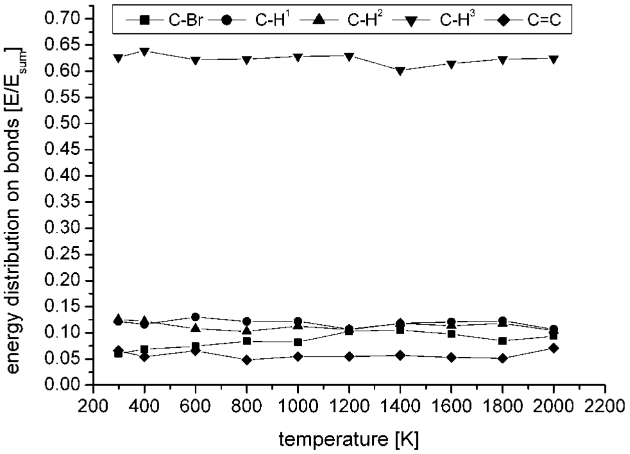

Figure 5. Vibrational energy distribution on the bonds of vinyl bromide in the dependence of the temperature. The frictional coefficient $\gamma = 0.3$.

The elimination of HBr from vinyl bromide assumes the bond breaking of CH and CBr bonds. On the basis of RRKM theory, if a bond has high kinetic energy, this can support the reaction channel in which the breaking of this bond is taking part. Because the breaking of the CBr bond is equally important in both the three-centered and four-centered HBr elimination, the CH bond breaking will be determined by the aspect of the dissociation channel. Because the results show that in the case of $\gamma = 0.3$ the kinetic energy concentrates on CH^3 bond, this situation seems to favor the four-center HBr elimination from the vinyl bromide molecule. To test this idea, the dissociation process by further Langevin dynamic calculations was examined. We have done a sum of 50 runs, 25−25 with and without frictional interaction. The $\gamma = 0$ and 0.3 and $\tau = 0.01$ ps values for the frictional coefficient and bath relaxation time were used, respectively. To indicate the molecular dissociation within an appropriate simulation time, the temperature was increased to 3000 K. Without friction, 18 out of 25 runs showed three-centered elimination. When the friction was switched on, only the four-center elimination occurred. This shows significant change in the distribution between the three- and four-center elimination channels. However, the low number of runs is not enough to estimate a given value of the efficiency.

Figure 6 shows the adequate bond lengths (CBr, CH^3, and HBr) plotted against the simulation time during dissociation of HBr from vinyl bromide, as an example. As the above-described dependence predicted, the four-center HBr elimination occurred very fast, and acetylene and HBr as products were formed. No other reaction pathways were found by repeating the simulation when the friction was switched on. This finding shows that under the above condition, simulated by the Langevin model using the above-described parametrization, the four-center HBr elimination from vinyl bromide molecule occurs with very high efficiency. This is in agreement with a recent experimental work where the increase of the rate of acetylene product formation has been obtained by increasing the pressure of Ar as the bath gas.[55]

The average total energy sampled after the heating phase was found to be 297 kJ/mol related to the total energy of relaxed

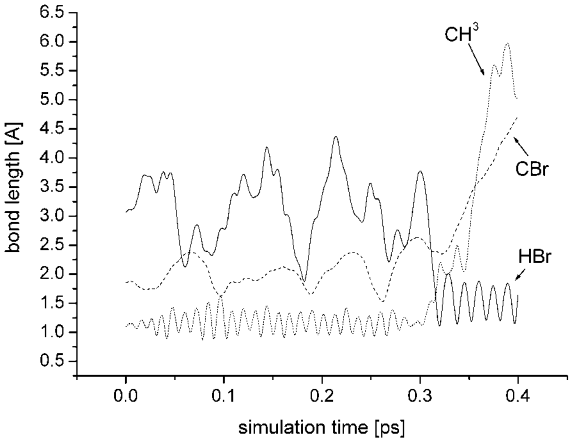

Figure 6. Mechanistic details for the four-center HBr elimination reaction. The plot shows the temporal variations of the C−Br, C−H^3, and H^3−Br distances during the dissociation process.

vinyl bromide at 0K. The maximum deviation of the energy was found to be 54 kJ/mol. The AM1 molecular total energy in TS3 and TS4 transition states is estimated as 296 and 327 kJ/mol, respectively. This means that by the energetical point of view the vinyl bromide molecule could sample both the TS3 and TS4 states by its molecular vibrations. However, the CH^1 bond breaking (assumed to three-center elimination) seems to be blocked, whereas the CH^3 bond breaking (assumed to four-center elimination) is supported by the frictional interaction. As a result of this property, the three-center elimination channel is closed, and the four-centered elimination channel is opened for the dissociation of the molecule.

Conclusion

The effect of the molecular environment on the dissociative reactions of vinyl bromide was examined by the Langevin molecular dynamics method in the absence and presence of frictional interaction between the atoms of the molecule and its environment. The results show a redistribution of the vibrational energy on the bonds of vinyl bromide under the effect of frictional interaction. This redistribution can modify the dissociation pathways of vinyl bromide. (A similar effect of time-dependent vibrational energy redistribution has been suggested for the photolysis of vinyl bromide.[56]) When the frictional coupling between the vinyl bromide and its environment is increased, the vibrational energy redistribution increases the reaction rate of the four-center HBr elimination channel in agreement with the experiments.[55] These results suggest that the energetics of the reaction channels in different “inert” matrices needs a careful estimation.

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