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# Theoretical Study of the 5-Aminotetrazole Thermal Decomposition

Vitaly G. Kiselev and Nina P. Gritsan\*

*Institute of Chemical Kinetics and Combustion, Siberian Branch of the Russian Academy of Sciences, 3 Institutskaya Street, 630090 Novosibirsk, Russia, and Novosibirsk State University, 2 Pirogova Street, 630090 Novosibirsk, Russia*

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The thermal decomposition of 5-aminotetrazole was studied theoretically using the G3 multilevel procedure and DFT B3LYP technique. The unimolecular primary decomposition reactions of the three most stable isomers of 5-ATZ were studied in the gas phase and in the melt using a simplified model of the latter. The influence of the melt on the elementary reaction barrier was taken into account by the calculation of the solvation free energies using the PCM model. In contrast to all previous publications, we considered the bimolecular reactions of 5-ATZ and demonstrated that they are very important especially in the condensed phase. It was found that the imino form undergoes fast isomerization to the amino form in the H-bonded dimers and does not participate in the 5-ATZ thermolysis. On the contrary, amino and, probably, the 2H isomer are the main isomers of 5-ATZ in the melt and gas phase. The N<sub>2</sub> elimination reaction was found to be the dominant unimolecular channel of the amino and 2H isomer decomposition in both the gas phase and melt. The significant lowering of the activation barriers of decomposition reactions in H-bonded dimers was found. In agreement with the existing experimental data, HN<sub>3</sub> elimination dominates for some of the considered complexes. It was concluded that the initial stages of thermolysis of 5-ATZ cannot be satisfactorily described by the simple unimolecular reactions proposed in the literature.

## Introduction

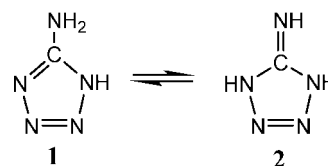
5-Aminotetrazole (5-ATZ) is of significant interest for combustion chemistry as a burn rate modifier and fire suppressor.<sup>1–6</sup> Due to its thermal stability, nonexplosive character, and high nitrogen content, 5-ATZ is an environmentally friendly gas-generator agent.<sup>7–10</sup> Some derivatives of 5-ATZ are also promising high-energy materials.<sup>11</sup> The alkali metal salts of the 5-aminotetrazolate anion are interesting for environmentally friendly pyrotechnics.<sup>12,13</sup> In addition, tetrazole and its derivatives are widely used as ligands in organometallic chemistry.<sup>14–17</sup> Even though the thermal decomposition of 5-ATZ has been intensively studied under different conditions, there are still some contradictory assumptions concerning the initial reactions of its thermolysis.

At room temperature, 5-ATZ is crystalline; its melting point is 205–207 °C.<sup>3,18,19</sup> The amino–imino tautomerism (Scheme 1) is typical of tetrazole and its derivatives.<sup>20,21</sup> However, there is no certain information about tautomeric equilibrium of 5-ATZ in the crystal and liquid states.

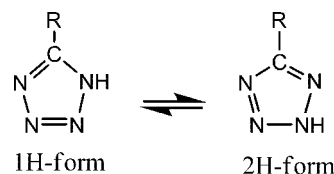
The authors of the early work<sup>22</sup> analyzed UV and IR spectra of solid 5-ATZ and concluded that it exists mainly in the amino form **1**. This statement was questioned in the 1970s. It was found, based primarily on the IR and Raman spectroscopy,<sup>23,24</sup> that the imino form **2** prevails in the solid state of 5-ATZ. On the other hand, it was concluded later that 5-ATZ exists in the amino form in solution.<sup>21,25</sup> The tautomeric equilibrium in substituted 5-ATZ was also found to be strongly dependent on the phase, nature of the substituent, and its position.<sup>21</sup>

Furthermore, the annular 1H–2H tautomerism (Scheme 2) is also a controversial issue in the tetrazole chemistry.<sup>21</sup> The NMR studies<sup>26,27</sup> showed the predominance of the 1H form

SCHEME 1



SCHEME 2

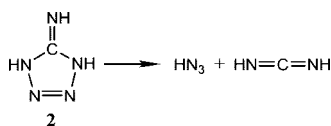


(Scheme 2, R = H) in dimethylformamide and acetone solutions. However, the analysis of ionization constants of 5-substituted tetrazoles<sup>28</sup> showed that the 2H form (Scheme 2) is preferable in the water solution of these compounds. It was suggested, on the basis of the microwave spectroscopy,<sup>29</sup> that tetrazole exists mainly in the 2H form in the gas phase. To the best of our knowledge, the 1H–2H tautomerism in 5-ATZ system has never been studied.

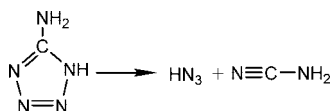
Lesnikovich et al.<sup>18,19</sup> pointed out the importance of the amino–imino tautomeric transformations (Scheme 1) in the mechanism of 5-ATZ decomposition. On the basis of the analysis of the IR spectra of initial and thermally treated samples, the authors concluded that in the crystal state, 5-ATZ exists mainly in the thermodynamically less favorable imino form **2**. Melting or evaporation of the sample resulted in an increase of the content of amino form **1**. They also investigated thermal decomposition of 5-ATZ using the IR and mass spectrometric analysis of the product mixture.<sup>19</sup> It was found that the decomposition started at the temperatures slightly higher than the

\* To whom correspondence should be addressed. Tel: 7 (383) 333 3053. Fax: 7 (383) 330 7350. E-mail: gritsan@kinetics.nsc.ru.

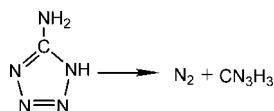
## SCHEME 3



## SCHEME 4



## SCHEME 5



melting point of the sample. The  $\text{N}_2$ ,  $\text{HN}_3$ , and  $\text{NH}_3$  were determined to be the major gaseous products. The  $\text{NH}_4\text{N}_3$  and melamine ( $\text{C}_3\text{H}_3\text{N}_6$ ) were detected as volatile condensed products. It was proposed,<sup>18,19</sup> that the imino form **2** decomposes mainly via elimination of  $\text{HN}_3$  (Scheme 3).

At the same time, heating and subsequent melting lead to the isomerization of **2** to the more stable amino form **1**, which decomposes in accordance with Schemes 4 and 5.

The kinetics of the 5-ATZ thermolysis was described as a first-order process with the activation energy decreasing from  $\sim 50$  kcal/mol at the initial stage to the value of  $\sim 35$  kcal/mol in the middle of the decomposition process.<sup>19</sup> The pre-exponential factor varied from  $\log A = 11.8$  to 13.7.

In contrast to the conclusion of Lesnikovich et al.,<sup>18,19</sup> Brill et al.<sup>3,30</sup> implicitly presumed that 5-ATZ exists exclusively in the amino form **1**. In the T-jump/FTIR experiments, the authors<sup>3,30</sup> identified a significant amount of the  $\text{HN}_3$  and  $\text{NH}_2\text{CN}$  at the early stage of 5-ATZ decomposition and attributed the disappearance of **1** completely to the reaction of Scheme 4. Melamine,  $\text{NH}_4\text{N}_3$ , and  $\text{HCN}$  were also detected at the later thermolysis stages. The temperature of the decomposition onset was found to be near the melting point, in agreement with results of Lesnikovich et al.<sup>18,19</sup>

In a very recent paper, Paletsky et al.<sup>31</sup> reported results of a mass spectrometric investigation of the 5-ATZ thermolysis. The major detected products were  $\text{HN}_3$ ,  $\text{N}_2$ , and  $\text{NH}_2\text{CN}$ . The  $\text{HCN}$ ,  $\text{NH}_3$ , melamine, and vaporized 5-ATZ were detected as well. On the basis of the measured time dependence of the product concentrations, the authors proposed the reactions of Schemes 3 and 5 to be the most important in the primary decomposition process. The corresponding Arrhenius parameters  $E_a \approx 25$  kcal/mol,  $\log A \approx 9.2$  for the former reaction (Scheme 3) and  $E_a \approx 31$  kcal/mol,  $\log A \approx 11.7$  for the latter one (Scheme 5) are significantly lower than the effective values obtained earlier for the overall process.<sup>18,19</sup> The average ratio of  $\text{HN}_3$  and  $\text{N}_2$  concentrations in the final product distribution was found to be 2:1. The same value was proposed for the 2/1 ratio in the sample of 5-ATZ during the decomposition process.

Thermodynamic characteristics of 5-ATZ and intermediates of its thermal decomposition and the rate constants of elementary reactions are crucial for modeling the complex thermolysis process. However, the existing experimental data on the primary reactions of the 5-ATZ thermal decomposition are incomplete and sometimes contradictory.<sup>3,18,19,30,31</sup> The  $\text{N}_2$ , being IR-inactive, has never been directly detected by spectroscopic methods. The line  $m/e = 28$  corresponding to the molecular nitrogen was

**TABLE 1: The Relative Gas-Phase Formation Enthalpies at 0 K ( $\Delta(\Delta H_{\text{gas}}^0)$ )<sup>a</sup> of the isomers 1–7, the Gas-Phase Formation Enthalpies at 298 K ( $\Delta_f H_{\text{gas}}^0$ ) Calculated at the G3 and B3LYP Levels and Measured Experimentally ( $\Delta_f H_{\text{gas}}^0$ , expt), and the Relative Free Energies of Solvation ( $\Delta(\Delta G_{\text{solv}}^0)$ )<sup>a</sup> Calculated Using the PCM Model at the B3LYP Level (all values in kcal/mol)**

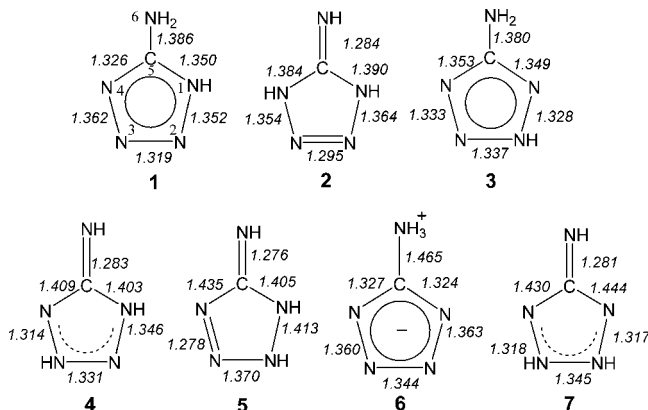
molecule	$\Delta(\Delta H_{\text{gas}}^0)$		$\Delta_f H_{\text{gas}}^0$		$\Delta(\Delta G_{\text{solv}}^0)$	$\Delta_f H_{\text{gas}}^0$ , expt
	G3	B3LYP	G3	B3LYP		
<b>1</b>	<b>0.0</b>	0.0	<b>81.5</b>	81.8	0.0	77.5 <sup>44,45</sup>
<b>2</b>	<b>10.7</b>	8.8	<b>92.4</b>	90.7	3.3	
<b>3</b>	<b>−2.8</b>	−3.0	<b>78.6</b>	78.7	3.4	
<b>4</b>	<b>25.5</b>	23.5	<b>106.8</b>	105.2	−0.8	
<b>5</b>	<b>27.9</b>	25.8	<b>109.2</b>	107.4	3.5	
<b>6</b>	<b>33.1</b>	36.1	<b>114.7</b>	118.0	−16.5	
<b>7</b>	<b>56.9</b>	55.9	<b>138.3</b>	137.8	−7.3	
$\text{NH}_2-\text{CN}$ <b>I3</b>			<b>33.1</b>	33.8		32.1 <sup>41</sup>
1H-tetrazole			<b>82.3</b>			78.3, <sup>44,45</sup> 79.9 <sup>44</sup>
2H-tetrazole			<b>80.4</b>			
1-Me-5-ATZ			<b>76.6</b>			72.3, <sup>45</sup> 74.9 <sup>45,46</sup>
2-Me-5-ATZ			<b>72.3</b>			71.4, <sup>45</sup> 72.4 <sup>45,46</sup>

<sup>a</sup> Amino form **1** was chosen as a reference compound for the calculation of relative thermodynamic properties.

found in the mass spectrum of the 5-ATZ thermolysis products.<sup>19,31</sup> However, it remains unclear whether this  $\text{N}_2$  is the primary product or the product of  $\text{HN}_3$  electronic impact destruction. Since the distribution of the primary reaction products cannot be measured directly and the information about the tautomeric equilibrium of **1**–**3** (Schemes 1 and 2) is lacking, the proposed mechanisms are, to some extent, speculative. A number of different pathways and key intermediates of the 5-ATZ thermolysis have been proposed so far, but they have not been sufficiently supported and substantiated. Moreover, the existing estimations of the activation barriers and rate constants of the elementary reactions are inconsistent. The problems in the measurement of the elementary reaction rate constants are mainly due to a significant number of fast simultaneous processes in the melt and gas phase with numerous short-lived intermediates involved. The experimental difficulties in the detection of some intermediates and products (e.g.,  $\text{N}_2$ ) are also a serious obstacle. Moreover, the kinetic measurements are hindered by the nonisothermal experimental conditions (e.g., the final product distribution depends on the heating rate).<sup>31</sup>

Quantum chemical calculations are the most appropriate alternative for obtaining thermodynamic and kinetic properties of the elementary reactions. To the best of our knowledge, the full mechanism of 5-ATZ thermolysis, including all possible intermediates and different pathways, has never been studied theoretically. Some reactions have only been studied using semiempirical methods,<sup>19</sup> ab initio approaches at a relatively low level of theory,<sup>18</sup> or common DFT methods.<sup>32,33</sup> The only reaction of Scheme 4 in the gas phase has been studied at a high level of theory.<sup>33</sup> However, the bimolecular reactions of 5-ATZ have never been considered in the literature.

The main goals of our paper are to investigate theoretically the thermodynamic properties of different possible isomers of 5-ATZ, to identify clearly the intermediates of their primary reactions, and, eventually, to give an insight into the mechanism of primary stages of the 5-ATZ thermal decomposition. The solid-state decomposition was found experimentally to be negligible for 5-ATZ; thermolysis proceeds in the melt and gas phase.<sup>3,18,19</sup> Therefore, we calculated the rate constants of the primary reactions in the gas phase and in the melt using a simplified model of the latter. In contrast to all previous publications, we considered the bimolecular reactions of 5-ATZ



**Figure 1.** Bond lengths (in Å) of the different isomers of 5-ATZ optimized at the MP2(Full)/6-31G(d) level.

and demonstrated that they are very important especially in the condensed phase.

### Computational Details

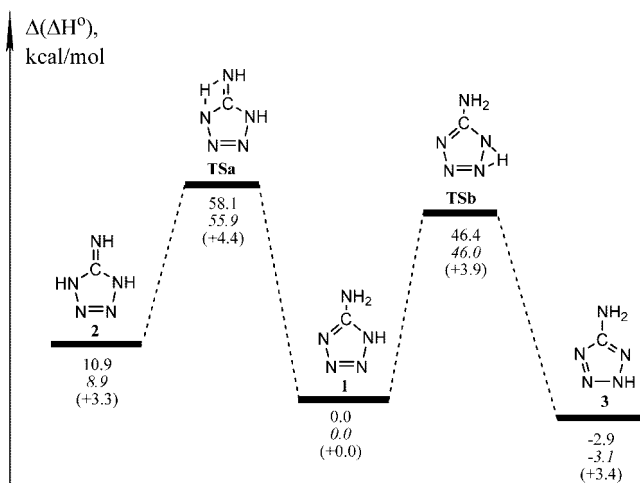
All thermochemical data as well as barriers of unimolecular reactions of different 5-ATZ isomers have been calculated using the Pople group's G3 method.<sup>34</sup> Earlier, we demonstrated a good performance of this procedure for thermochemical calculations in C-, N-, and O-containing systems.<sup>35</sup> In order to test the accuracy of the DFT B3LYP/6-311G(d,p) procedure, all of these values were also obtained by this method. The latter technique has been applied for the study of the bimolecular reactions of the 5-ATZ isomers. All of the equilibrium and transition state structures were ascertained to be the minima and saddle points, accordingly, on the potential energy surfaces. The corresponding thermal corrections were included in order to obtain the enthalpy and Gibbs free energy values at the desirable temperature. The free energies of solvation were calculated using the PCM model<sup>36,37</sup> and aniline as a solvent at the B3LYP/6-311G(d,p) level of theory.<sup>38,39</sup> All quantum chemical computations were performed using the Gaussian 03<sup>40</sup> suite of programs.

The gas-phase enthalpies of formation (at  $p = 1$  atm and  $T = 298$  K,  $\Delta_f H_{\text{gas}}^0$ ) were obtained using the atomization energy approach; the calculated atomization energies at 298 K were subtracted from the well-known enthalpies of formation of the isolated atoms. For any molecule M, the enthalpy of formation was calculated as follows:

$$\Delta_f H_{\text{gas}}^0(\text{M}) = E_{\text{el}}(\text{M}) + \text{ZPVE}(\text{M}) + [H_{298}(\text{M}) - H_0(\text{M})] - \sum_i^{\text{atoms}} \{E_{\text{el}}(\text{X}_i) + [H_{298}(\text{X}_i) - H_0(\text{X}_i)]\} + \sum_i^{\text{atoms}} \Delta_f H_{\text{gas}}^0(\text{X}_i)$$

where  $E_{\text{el}}(\text{M})$  is the electronic energy of the molecule calculated at the chosen level of theory;  $E_{\text{el}}(\text{X})$  is the electronic energy of the atom  $\text{X}_i$  calculated using the same technique; ZPVE is the energy of molecule's zero-point vibrations;  $[H_{298}(\text{M}) - H_0(\text{M})]$  is a thermal correction to the enthalpy obtained by means of simple Gibbs' statistical mechanics. The NIST Chemistry webbook<sup>41</sup> was used as a source of the atomic enthalpies  $\Delta_f H_{\text{gas}}^0(\text{X}_i)$ .

The influence of the melt on the thermochemistry and rate constants was taken into account by the calculation of the free



**Figure 2.** The relative gas-phase enthalpies of the stationary points on the PES for the monomolecular interconversion of isomers 1–3 calculated at the G3 (normal font) and B3LYP (italics) levels of theory. The relative free energies of solvation calculated using the PCM model are presented in parentheses. Amino form 1 was chosen as a reference compound for the calculations of relative thermodynamic properties. All values are in kcal/mol.

energies of solvation. Aniline was chosen as a solvent in our model calculations. In our opinion, the properties of this typical aromatic amino compound fit well those of 5-ATZ. Furthermore, aniline is fully parametrized for the application as a solvent in the calculations using the PCM model.<sup>36,37</sup> Apart from the usage of this simplified model, we considered some bimolecular reactions of the compounds under study, which could easily proceed in the melt.

The rate constants of monomolecular reactions in the gas phase at a high-pressure limit and in the liquid state were computed in accordance with the canonical transition state theory (TST)<sup>42</sup>

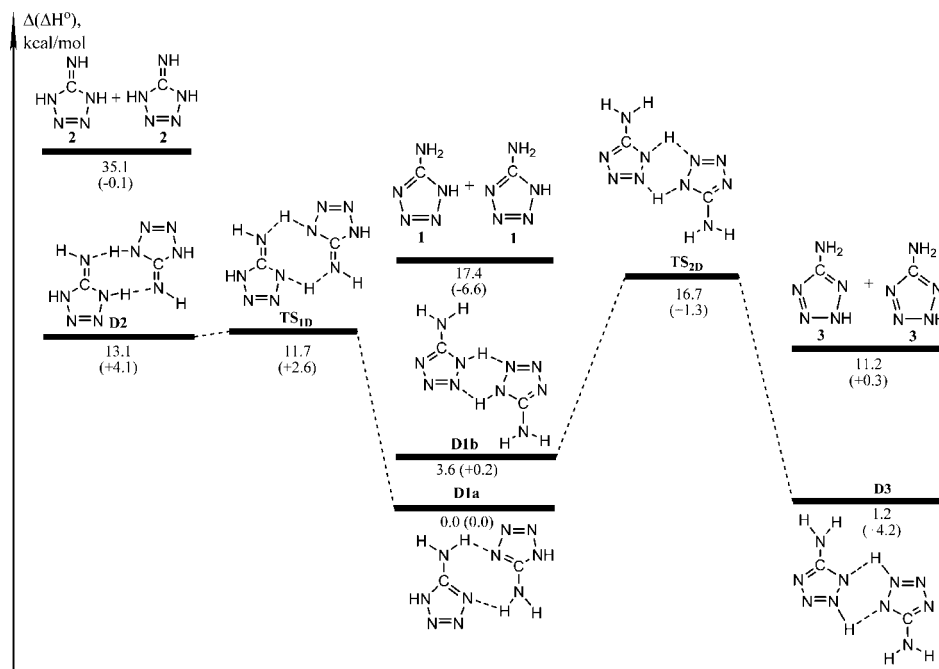
$$k(T) = \alpha \frac{kT}{h} \exp\left(-\frac{\Delta G^\ddagger(T)}{kT}\right) \quad (1)$$

where  $\alpha$  is a statistical factor (a number of equivalent reaction channels) and  $\Delta G^\ddagger$  is a free energy of activation calculated using the G3 electronic energy and corresponding thermal corrections (for the liquid state, the computed free energy of solvation was taken into account). The TST rate constants were calculated in the temperature range of 300–750 K with a step of 150 K and then approximated by the Arrhenius equation

$$k = A \exp(-E_a/RT) \quad (2)$$

### Results and Discussion

**1. Calculations of the Structure and Formation Enthalpies of Isomeric Forms of 5-ATZ.** Seven different isomeric forms of 5-ATZ (Figure 1, structures 1–7) could be proposed. Some of these isomers have two or more conformations. Geometries of all conformers have been optimized, and their enthalpies of formation have been calculated. However, only properties of the lowest-energy conformers are discussed in this paper. Figure 1 represents geometries of the species optimized at the MP2(Full)/6-31G(d) level (in the framework of the G3 procedure). The full structure description of all studied species is available in the Supporting Information.



**Figure 3.** The relative gas-phase enthalpies of the H-bonded dimers formed by isomers 1–3 calculated at the B3LYP level of theory. The relative free energies of solvation calculated using the PCM model at the B3LYP level are presented in parentheses. The dimer of the amino forms (**D1a**) was chosen as a reference species for the calculations of relative thermodynamic properties. All values are in kcal/mol.

The tetrazole ring was found to be planar for all considered compounds (1–7). The annular hydrogen atoms lie in the plane of the tetrazole ring, with the only exception of species 5, where H atoms deviate significantly from the plane to the opposite directions. Unfortunately, the experimental crystallographic data exist only for the 5-ATZ monohydrate.<sup>43</sup> In this crystal, the 5-ATZ was found to exist in the amino form,<sup>43</sup> although the N<sub>2</sub>–N<sub>3</sub> experimental bond length (1.280 Å) is closer to the calculated one for the imino form 2 and the measured C–N<sub>6</sub> bond length (1.330 Å) lies between the computed values for 1 and 2.

The calculated gas-phase formation enthalpies ( $\Delta_f H^\circ_{\text{gas}}$ ), the relative enthalpies at 0 K, and solvation free energies for the isomers 1–7 are presented in Table 1. In addition, for the purpose of testing the reliability of the method employed, this table contains the calculated  $\Delta_f H^\circ_{\text{gas}}$  values of some species (cyanamide **I3** and different tetrazole derivatives) with the known experimental enthalpies of formation. Unfortunately, the existing experimental data are rather scarce. Moreover, since the standard state of all of these compounds is crystal, the listed gas-phase formation enthalpies are the sum of two experimental values, the solid-state heat of formation and the sublimation enthalpy.

As mentioned in the Introduction, the tetrazoles are liable to annular 1H–2H tautomerism, and a more preferable form depends strongly on the phase and solvent.<sup>21</sup> The calculated  $\Delta_f H^\circ_{\text{gas}}$  value of 2H-tetrazole is lower than that of the 1H isomer and coincides better with experimental values. This fact might be an indication of the domination of the 2H-tetrazole form in the gas phase. The other G3 values are in reasonable agreement (within 1.5 kcal/mol) with the experimental data. Therefore, one can conclude that the G3 method is suited well for the study of tetrazole derivatives. At the same time, the B3LYP method also performs quite well; the deviation from the corresponding G3 results lies within 2 kcal/mol, with the only exception of the highly polar compound 6.

There exists only one paper devoted to experimental determination of the 5-ATZ gas-phase formation enthalpy.<sup>45</sup> The

authors combined the measured sublimation enthalpy ( $\Delta_{\text{sub}} H^\circ = 27.8$  kcal/mol) with the known formation enthalpy of the solid 5-ATZ ( $\Delta_f H^\circ_{\text{solid}} = 49.7$  kcal/mol).<sup>44</sup> The resulting value  $\Delta_f H^\circ_{\text{gas}} = 77.5$  kcal/mol is 4 kcal/mol lower than the G3 prediction for 1. However, this value is reported only in one paper, and the isomeric composition of 5-ATZ, as stated above, is not well-known. Note that the experimental value is closer to the G3 prediction for the isomer 3 ( $\Delta_f H^\circ_{\text{gas}} = 78.6$  kcal/mol), which is also found to be the most preferable isomer in the gas phase.

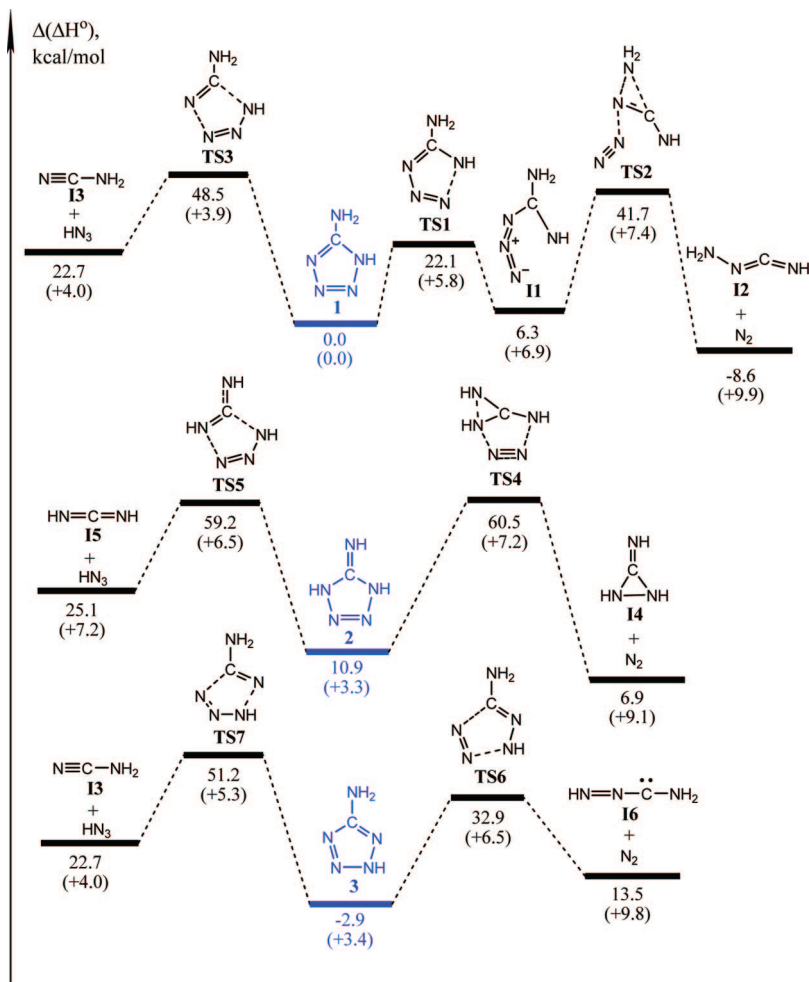
Although 2H form 3 is predicted to be the most stable gas-phase isomer, the enthalpy difference between 1 and 3 is relatively small (2.8 kcal/mol at 0 K). In the melt, on the contrary, 1 is predicted to lie slightly lower in energy than 3 (by about 0.5 kcal/mol). The imino form 2, due to the lack of aromaticity in the tetrazole ring, is predicted to be significantly less favorable than 1 and 3 (by about 10 kcal/mol) in both the gas phase and melt. The relative formation enthalpies of the isomers 4–7 are considerably higher than those of 1–3. Note that for the highly polar species 6 and 7, the account of solvation reduces significantly their relative enthalpy and free energy. Nevertheless, the isomers 4–7 remain thermodynamically unfavorable in the gas phase and melt.

**2. Mutual Interconversion of the Isomers 1–3.** As mentioned in the Introduction, the information available on the tautomeric equilibrium of 5-ATZ in the melt and gas phase is contradictory.<sup>18–21</sup> Thus, we investigated the isomerization reactions of different forms of 5-ATZ. As the isomers 4–7 are thermodynamically very unfavorable, we studied in detail only reactions of compounds 1–3.

Figure 2 demonstrates the stationary points on the PES for the monomolecular interconversion between isomers 1–3. It is seen that the activation barriers for all monomolecular isomerization reactions are very high in both the gas phase and melt.

However, it is clear that 5-ATZ in all isomeric forms could form hydrogen-bonded complexes. As an example, Figure 3 demonstrates structures of a few H-bonded complexes (**D1–D3**).





**Figure 4.** The relative gas-phase enthalpies of the stationary points on the PES for the decomposition of isomers **1**–**3** calculated at the G3 level of theory. The relative free energies of solvation calculated using the PCM model at the B3LYP level are presented in parentheses. Amino form **1** was chosen as a reference compound for the calculations of relative thermodynamic properties. All values are in kcal/mol.

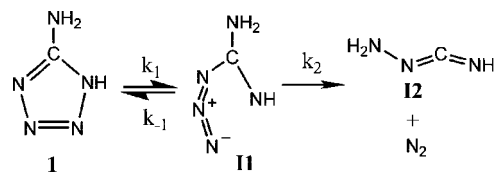
It is seen from Figure 3 that concerted double hydrogen transfer in the H-bonded complexes leads to their interconversion. We studied these concerted reactions using the B3LYP technique since the application of the G3 method requires significant computational resources in this case. Table 1 demonstrates that the B3LYP technique gives sufficiently accurate results for the 5-ATZ system.

The dimer **D1a** formed by two molecules of **1** turned out to be the most thermodynamically stable. The dimer **D2** formed by two imino forms **2** is less favorable and is prone to isomerization to **D1a**. The barrier for this transformation is very low, taking the thermal corrections into account drops the enthalpy of the transition state **TS<sub>2D</sub>** below that of **D2**. Thus, this reaction is predicted to be barrierless. Therefore, even if the imino form **2** prevails in the crystal state of 5-ATZ,<sup>23,24</sup> melting should lead to a very fast isomerization of **2** to **1** due to the reaction of hydrogen transfer in the H-bonded complexes.

We considered also conversion of the H-bonded complex of **1** (**D1b**, Figure 3) to the complex of the 2H forms **3** (**D3**). The barrier for this reaction is noticeably higher (~13 kcal/mol), but it is still significantly lower than the barrier for the unimolecular isomerization.

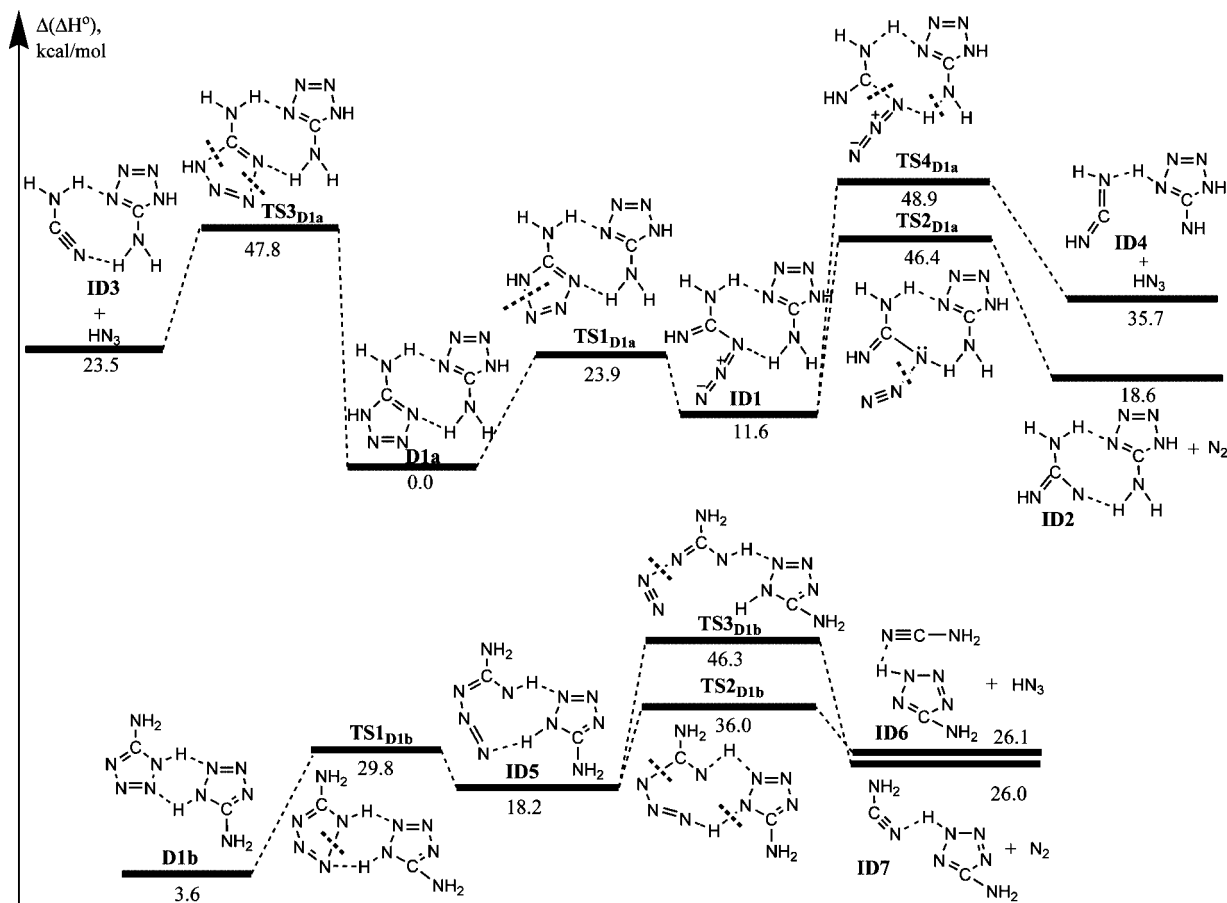
It is obvious that the real structure of the melt and processes taking place upon melting are much more complicated than our simple model. Nevertheless, even simple consideration of the reactions in the H-bonded dimers leads to the conclusion that

#### SCHEME 6



the content of imino form **2** in the melt and gas phase is negligible, and the reaction of Scheme 3 is most likely unimportant for the 5-ATZ decomposition.

**3. Monomolecular Reactions of the Thermal Decomposition of 5-ATZ.** Although the importance of the bimolecular processes and reactions in the H-bonded complexes was demonstrated above, we will consider first the monomolecular reactions of the 5-ATZ decomposition (Schemes 3–5). The stationary points on the PES corresponding to the lowest unimolecular decomposition channels of **1**, **2**, and **3** are shown in Figure 4. For all isomers, two competing primary channels are the  $\text{HN}_3$  and  $\text{N}_2$  elimination reactions. Apart from the activation enthalpies depicted in Figure 4, we calculated the rate constants for these channels in the temperature range of 300–750 K using TST (formula 1). The results were approximated by the Arrhenius equation (eq 2), and the calculated Arrhenius parameters were summarized in the Supporting Information (Table S1). The rate constant of the reaction of Scheme 4 has been calculated recently at high levels of theory



**Figure 5.** The relative gas-phase enthalpies of the stationary points on the PES for the decomposition of H-bonded complexes **D1a** and **D1b** calculated at the B3LYP level of theory. The dimer **D1a** was chosen as a reference species for the calculations of relative thermodynamic properties. All values are in kcal/mol.

(CCSD(T) and QCISD(T)), although the basis sets of a moderate size were employed.<sup>33</sup> Results of these calculations are close to our data.

The most kinetically preferable monomolecular decomposition channels of the isomers **1** and **3** lead to the formation of  $N_2$  (Figure 4). In the case of **1**, the monomolecular reaction of  $N_2$  elimination is a two-step process (Scheme 6). The first step is the ring-opening reaction with formation of azide intermediate **I1**. Then, the azide **I1** decomposes through the elimination of  $N_2$  with simultaneous insertion of another nitrogen atom into the C–NH<sub>2</sub> bond. Note that this reaction resembles the Curtius rearrangement of the carbonyl azides, which also proceeds as a concerted process without intermediacy of nitrene.<sup>47–49</sup>

The decomposition pathways of 2H form **3** (Figure 4, bottom) are similar to those of **1** (Figure 4, top). However, in contrast to **1**, the reaction of  $N_2$  elimination is a one-step process. The barrier of this reaction in the gas phase is 35.8 kcal/mol. This is much lower (nearly by 20 kcal/mol) than the barrier of the HN<sub>3</sub> elimination reaction. The byproduct of the  $N_2$  elimination reaction is a carbene **I6**. This compound has a singlet ground state with the singlet–triplet splitting of 28.9 kcal/mol.

As shown in the previous section, the content of imino form **2** in the melt and gas phase is negligible; nevertheless, we considered reactions of this isomer too. Unlike the **1** and **3** cases, the HN<sub>3</sub> elimination reaction is more preferable for the imino form **2**. Its gas-phase barrier (48.3 kcal/mol) is slightly lower than that (49.6 kcal/mol) of the  $N_2$  elimination reaction. The products of the former reaction are HN<sub>3</sub> and carbodiimide **I5**. 3-Imino-diaziridin **I4** is formed in the latter concerted reaction

of  $N_2$  elimination. As proposed previously,<sup>18,19,31</sup> the imino form **2** is the only isomer of 5-ATZ whose monomolecular decomposition yields preferentially HN<sub>3</sub>.

For the sake of further comparison, we recalculated the activation enthalpies of the decomposition reactions of **1–3** at the B3LYP level of theory (Figure S1, Supporting Information). Comparison of Figures 4 and S1 (Supporting Information) demonstrates that the results of the B3LYP calculations deviate only slightly ( $\sim 2$  kcal/mol) from those of the G3 calculations.

Our previous discussion is based on the enthalpy considerations, although the rate constants of the monomolecular reactions are determined by a free energy of activation (eq 1). The relative Gibbs free energies of the stationary points on the PES corresponding to the lowest monomolecular decomposition channels of **1–3** are displayed in Figure S2 (Supporting Information). Comparison of Figures 4 and S2 (Supporting Information) demonstrates that the same conclusion on the dominant reactions of **1–3** could be made on the basis of the free energy consideration.

Taking the solvation energy into account affects the calculated barriers (and rate constants) of the monomolecular reactions (Figure 4, Table S1, Supporting Information) noticeably. For the proposed model of the melt, the calculated barriers of nearly all of the considered reactions will increase compared to the gas phase by a few kcal/mol.

#### 4. Decomposition Reactions in the H-Bonded Complexes.

As the isomers **1–3** are liable to form H-bonded complexes, we analyzed the decomposition reactions in selected complexes. It should be noted that dozens of different complexes

of **1–3** and primary products of their decomposition could be proposed. We studied in detail only some of them in order to show important distinctions from the conventional single-molecule consideration (e.g., Schemes 3–5). As an example, Figure 5 demonstrates the decomposition channels for two types of amino form dimers (**D1a** and **D1b**). The relative Gibbs free energies of corresponding PES points are given in the Supporting Information (Figure S3).

We compared then the reactions of  $N_2$  and  $HN_3$  elimination proceeding in the free molecule (Figure 4, top; see also Figure S1, Supporting Information, for the calculations at the B3LYP level) and in the H-bonded dimer **D1a** (Figure 5, top). First of all, the complex formation influences the barriers of the reactions of  $N_2$  and  $HN_3$  elimination (**TS2** and **TS3**), making them much closer in energy (Figure 5, top) than those in the case of monomolecular reactions (Figure 4, top; see also Figure S1, top, Supporting Information). In addition, a new channel of decomposition arises in the dimer, namely, formation of  $HN_3$  in the reaction of **ID1** (**TS4<sub>D1a</sub>**) involving hydrogen atom transfer between molecules.

Results of the calculations for the **D1b** complex (Figure 5, bottom) demonstrate that the new channel of  $HN_3$  elimination (**TS2<sub>D1b</sub>**) involving intermolecular hydrogen transfer has an even lower barrier than that of  $N_2$  elimination (**TS3<sub>D1b</sub>**). Results for the decomposition of the dimer **D3** are presented in the Supporting Information (Figure S4). Therefore, formation of the H-bonded dimers is very important for the 5-ATZ thermal decomposition.

## Conclusion

On the basis of the results of our calculations, the following remarks on the mechanism of the 5-ATZ thermal decomposition can be made. The imino form **2** is prone to the fast bimolecular transformation to the more thermodynamically preferable amino isomer **1** (Figure 3). Thus, in contrast to the previous assumptions,<sup>18,19,31</sup> the calculations suggest that the imino form **2** is not important in the chemistry of 5-ATZ decomposition in both the melt and gas phase and 5-ATZ exists mainly in the thermodynamically more preferable **1** and **3** forms.

Results of our calculations for the monomolecular reactions of 5-ATZ decomposition (Figure 4) agree with the previous assumption<sup>18,19</sup> that **2** is the only 5-ATZ isomer whose monomolecular decomposition in the gas phase leads to the  $HN_3$  formation. The monomolecular reactions of the forms **1** and **3** yield preferentially  $N_2$  in the gas phase. The account of the melt by means of the simple PCM model does not change this tendency.

It is well-established that  $HN_3$  along with  $N_2$  are the primary products of 5-ATZ thermal decomposition.<sup>3,18,19,31</sup> On the basis of our calculations (Figure 5), we can give new explanation of this result, namely, that formation of  $HN_3$  becomes more preferable in some bimolecular reactions of form **1**. In our opinion, the commonly accepted consideration of the initial stage of the 5-ATZ thermal decomposition taking into account only monomolecular processes (Schemes 3–5)<sup>3,18,19,31</sup> is not appropriate. A correct description can be attained only by account of the formation of H-bonded complexes and their subsequent decomposition. In this paper, we considered only selected dimers and their reactions. Nevertheless, new channels of decomposition involving intermolecular hydrogen transfer have been found. The barriers of these new reactions are lower than the barriers of the monomolecular processes considered previously (Schemes 3–5). Therefore, the effective activation energy of the 5-ATZ thermal decomposition is noticeably lower than the correspond-

ing values for the monomolecular reactions of Schemes 3–5. Unfortunately, the real situation, especially in the melt, is very complicated and does not allow direct comparison of the calculated and experimental results. Moreover, all available experimental results<sup>3,18,19,31</sup> were obtained under strong nonisothermal conditions; therefore, even the activation energy and pre-exponential factor are not unambiguously defined. For instance, the authors of the recent paper<sup>31</sup> reported low activation energies for the reactions of  $HN_3$  and  $N_2$  formation (25.6 and 31.6 kcal/mol, respectively). However, the big difference between the activation energies is almost completely compensated for by the difference in the pre-exponential factors; therefore, the rate constants of  $HN_3$  and  $N_2$  formation are nearly equal.<sup>31</sup> Moreover, the activation energy was found to change significantly even during the initial stage of the 5-ATZ decomposition.<sup>18,19</sup> The product composition was also found to be strongly dependent on the type of reactor<sup>19,31</sup> and heating rate.<sup>31</sup>

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**Supporting Information Available:** Cartesian coordinates of all compounds under study. Calculated Arrhenius parameters for the monomolecular decomposition reactions (Table S1), relative enthalpies of the stationary points on the PES for the monomolecular reactions of **1–3** species calculated at the B3LYP level (Figure S1), Gibbs free energy surface for the same reactions calculated at the G3 level (Figure S2), Gibbs free energy surface for the decomposition reactions of **D1a** and **D1b** dimers (Figure S3), and relative enthalpies of the stationary points on the PES (Figure S4) for the decomposition reactions of **D3** dimer (pdf file). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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