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Unexpected Primary Reactions for Thermolysis of 1,1-Diamino-2,2-dinitroethylene (FOX-7) Revealed by *ab Initio* Calculations

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Ⓢ *Supporting Information*

ABSTRACT: The primary thermolysis reactions of a promising insensitive explosive 1,1-diamino-2,2-dinitroethylene (DADNE, FOX-7) have been studied in the gas phase at a high level of theory (CCSD(T)-F12/aVTZ). Our calculations revealed that none of the conventional reactions ($C-NO_2$ bond fission, nitro-nitrite and nitro-aci-nitro rearrangements) dominate thermolysis of FOX-7. On the contrary, two new decomposition pathways specific for this particular species that commenced with enamino–imino isomerization and intramolecular cyclization were found instead to be more feasible energetically. The activation barriers of these primary isomerization reactions were calculated to be 48.4 and 28.8 kcal/mol, while the activation energies of the overall decomposition pathways are predicted to be ~49 and ~56 kcal/mol, respectively. The new pathways can also be relevant for a wide series of unsaturated hydrocarbons substituted with both nitro- and amino-groups (e.g., triaminotrinitrobenzene, TATB).

FOX-7 (DADNE)
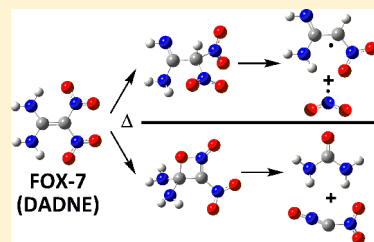
INTRODUCTION

Development of high-performance explosives with low sensitivity to impact and friction and good thermal stability is a subject of intense ongoing research worldwide.[1−5] 1,1-Diamino-2,2-dinitroethylene (DADNE, FOX-7), first synthesized in 1998, is among the most promising insensitive energetic compounds.[6,7] While its performance is comparable to hexogen (RDX), DADNE (**1**) is profoundly less sensitive.[6,8] Note that the $C-NO_2$ bond strength and some closely related parameters have mainly been invoked to establish empirical correlations and, ultimately, to rationalize the sensitivity trends of **1** among other nitroaromatics and nitroalkanes.[9−14] Significant efforts have also been made toward the design of scalable synthetic procedures and more efficient formulations of **1** with energetic binders.[15−17] Moreover, **1** is a widely used building block for a huge family of novel high-energy compounds.[18−22] Apart from being interesting per se, DADNE is a prototype of triaminotrinitrobenzene (TATB), a widely used commercial insensitive high explosive.

Even though the thermal decomposition of **1** has been intensively studied experimentally and theoretically, both kinetics and the mechanism of initial stages of thermolysis still remain unclear. Note that differential scanning calorimetry (DSC) and thermogravimetry/differential thermal analysis (TG/DTA) measurements performed by several independent groups yielded profoundly different results. Namely, on the basis of DSC measurements (210−250 °C), Ostmark et al. estimated the activation energy of the primary stage of **1** decomposition to be 56−58 kcal/mol.[23,24] Although the reaction order and preexponential factor were not determined and the results were found to be strongly dependent on the grain size in a sample,[24] the latter value is widely cited throughout the literature.[25−28] On the other hand, de Klerk et al.[29] found the average Arrhenius parameters to be E_a = 80.8 kcal/mol and $\log(A/s^{-1})$ = 38.1 from TG/DTA in the wide temperature range (~100−300 °C) and at various heating rates (from 2 to 10 °C/min). On the basis of both nonisothermal (190−270 °C) and isothermal TG measurements (190−200 °C), Teipel et al.[30] proposed two parallel reactions of noninteger orders $n_1 \approx 2.85$ and $n_2 \approx 0.46$ with the Arrhenius parameters $E_1 \approx 60$ kcal/mol, $\log(A/s^{-1}) \approx 23$ and $E_2 \approx 73$ kcal/mol, $\log(A/s^{-1}) \approx 26$, correspondingly. Finally, Burnham et al.[31] performed isothermal TG/DTA measurements (190−205 °C) and found much lower activation energy E_a = 45.7 kcal/mol.[31] However, their DSC measurements[31] at the low heating rates (0.1−1.0 °C/min) yielded the activation energy E_a = 57.0 kcal/mol. Thus, it is clear that the available experimental data on the primary reactions of DADNE thermolysis are contradictory and provide no insight into the mechanism of the process. The chemical mechanism of initiation of **1** is often simply related to the "weakest" or "trigger" bond, i.e., $C-NO_2$ in the particular case.[27,28,32−34]

Quantum chemical calculations are the most appropriate alternative to study the mechanism of DADNE thermolysis. First computational studies[25,33,35] on the DADNE thermal decomposition considered solely gas phase reactions typical of nitroalkanes and nitroaromatics, viz., $C-NO_2$ bond cleavage and nitro-nitrite and nitro-aci-nitro isomerizations[36,37] (Scheme 1). On the basis of calculations, the DADNE decomposition was proposed to be initiated by a nitro-nitrite rearrangement (k_2, Scheme 1) with a density functional theory (DFT) calculated barrier of about 59 kcal/mol.[25]

Scheme 1. Kinetic Scheme of the Conventional Thermolysis Pathways of DADNE
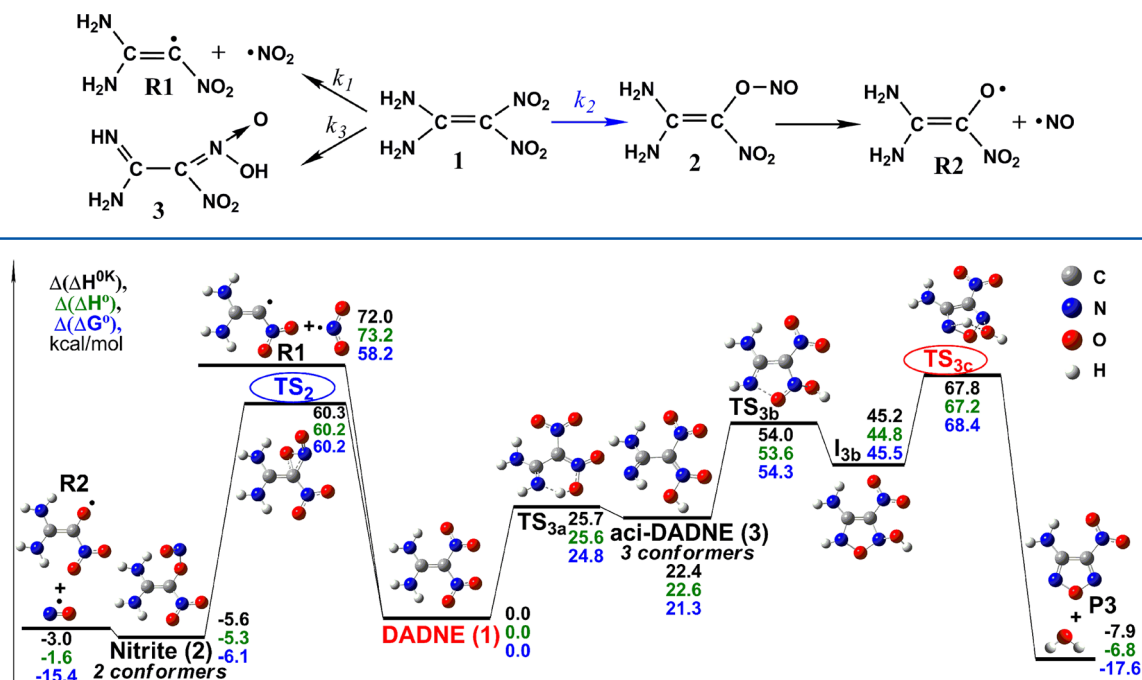

Figure 1. Relative thermodynamic properties of the stationary points on the PES corresponding to conventional reactions of thermal decomposition of DADNE (**1**): C−NO$_2$ bond cleavage (1), nitro-nitrite rearrangement (2), and isomerization to aci-form (3). Compound **1** was chosen as a reference compound for the calculations of relative thermodynamics. The two transition states (**TS$_2$** and **TS$_{3c}$**) corresponding to the rate-limiting steps of decomposition channels are encircled in blue and red color, respectively. All values are calculated at the CCSD(T)-F12b/aVTZ // M06-2X/6-311++G(2df,p) level of theory and are given in kilocalories per mole.

Subsequently, a series of pertinent solid state calculations more germane to experimental conditions were performed.[34,38−42] Note that similar typical reactions of the C−NO$_2$ bond cleavage and nitro-nitrite isomerization have been particularly scrutinized,[40,41] while the nitro-aci-nitro isomerization was proposed not to occur in the crystal.[39] These calculations revealed the pronounced effect of the crystalline environment on the rate constants of these reactions.[34,40] Moreover, the importance of shear strain and local defects for the kinetics of thermolysis of **1** has also been carefully elucidated.[34,38,40−42] Apart from this, very recently decomposition of DADNE from excited electronic states has been studied experimentally and theoretically (at the CASSCF and MP2 levels), and the •NO radical was found to be the most abundant primary product.[43]

Thus, in both the gas phase and solid state calculations the primary reactions typical of nitroalkanes and nitroaromatics have only been considered. However, the chemical structure of DADNE (a nitro enamine species) makes possible other reactions specific particularly for this compound and not discussed previously. Moreover, the simple structure of DADNE renders feasible the highly demanding modern post-Hartree−Fock quantum chemical techniques, which is, *inter alia*, important for obtaining reliable computational data and validation of computational results commonly provided by DFT. Therefore, the purpose of this work is to report the highly accurate quantum chemical study (CCSD(T)-F12/aVTZ) of the primary reactions of DADNE thermal decomposition in the gas phase. Particular attention has been paid to reactions *specific entirely for this nitro enamine compound*. Note that the gas phase calculations were motivated by the need to consider a variety of primary reactions of **1** in a more

complete fashion and to estimate their possible importance. Indeed, more sophisticated calculations in the solid state should be guided by appropriate understanding of relevant decomposition chemistry.

■ **COMPUTATIONAL METHODS**

Electronic structure calculations were carried out using the Gaussian 09[44] and Molpro 2010[45] program packages. The geometries of each structure corresponding to the stationary point on the potential energy surface (PES) of **1** decomposition were fully optimized using density functional theory at the M06-2X/6-311++G(2df,p) level.[46] Zero-point energies and thermal corrections to enthalpy and Gibbs free energy were computed at the same level of theory. Single-point electronic energies were afterward refined using an explicitly correlated coupled-cluster formalism CCSD(T)-F12b/aVTZ.[47] Note that the explicitly correlated F12 procedure accelerates the slow basis set convergence of conventional CCSD(T) techniques.[48] The extensive benchmarking on a series of decomposition reactions of polynitroalkanes, nitroethylene, and related species revealed a perfect agreement (within 0.5 kcal/mol) between the activation barrier values calculated using CCSD(T)-F12b/aVTZ, complete basis set extrapolated CCSD(T), and multilevel (W1 and G3)[49] procedures (Supporting Information, Table S1). On the basis of this benchmark, we infer that the CCSD(T)-F12b/aVTZ procedure provides a good balance between computational cost and accuracy. The multireference character of the wave functions of the reagents, intermediates, and transition states considered in the present work was estimated using the T1 diagnostic for the CCSD calculation.[50] Modest T1 values obtained in all cases (<0.025) indicate that a
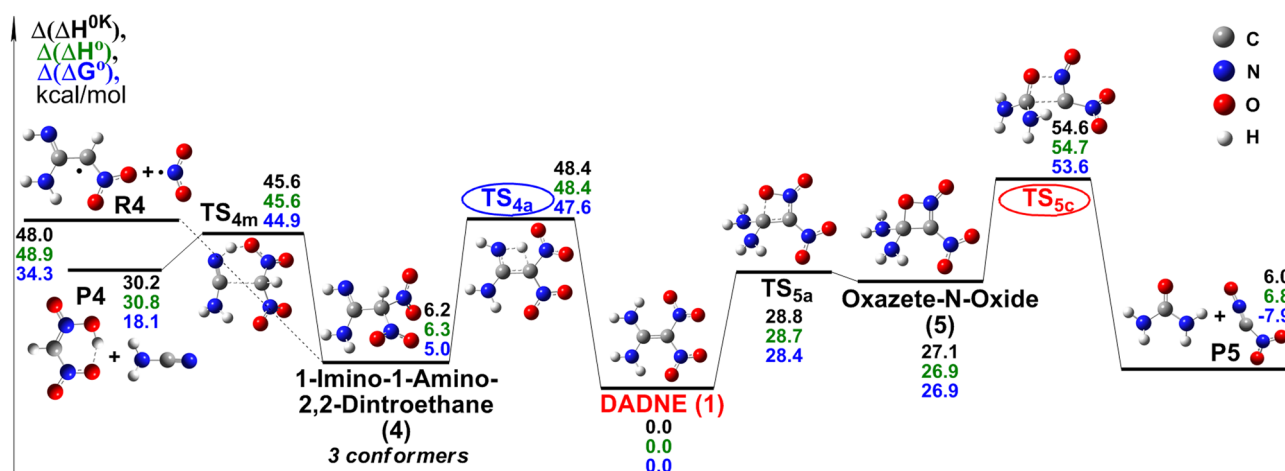
Figure 2. Two lowest energy thermal decomposition channels of DADNE (**1**). The two transition states (**TS$_{4a}$** and **TS$_{5c}$**) corresponding to the rate-limiting steps of decomposition channels are encircled in blue and red color, respectively. All values are calculated at the CCSD(T)-F12b/aVTZ// M06-2X/6-311++G(2df,p) level of theory and are given in kilocalories per mole.

Scheme 2. Kinetic scheme of the Enamino−Imino Isomerization of DADNE Followed by Molecular or Radical Decomposition (Pathway 4)^a
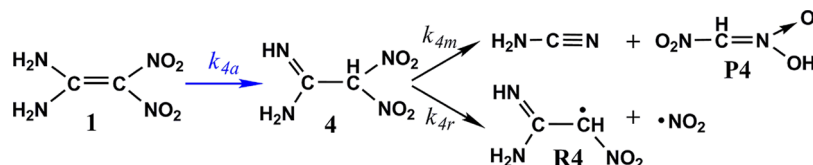
^{a}The rate-limiting stage is marked in blue.

single reference-based electron correlation procedure is appropriate in the present case.

The rate constants of monomolecular reactions in the gas phase at a high pressure limit were computed in accordance with the canonical transition state theory (TST):

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

where α is a statistical factor (a number of equivalent reaction channels) and $\Delta G^{\ddagger}$ is a free energy of activation calculated using the CCSD(T)-F12b/aVTZ electronic energy and corresponding M06-2X thermal corrections. The TST rate constants were calculated in the temperature range of 400−550 K with a step of 50 K and then approximated by the Arrhenius equation

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

RESULTS AND DISCUSSION

At first we examined the previously mentioned conventional decomposition channels of **1** at a high level of theory (Figure 1, Scheme 1). The C−NO$_2$ bond dissociation energy was found to be 72.0 kcal/mol in good agreement with previous computational estimations (70 kcal/mol at the B3P86 level[33] and ~73 kcal/mol according to G2-based estimations).[25] Note that D_0(C−NO$_2$) in dinitroalkanes is profoundly lower (e.g., ~49 kcal/mol in dinitromethane and *gem*-dinitroethane).[49,51] The higher stability of **1** might be attributed to conjugation between the π orbital of a double C=C bond and lone pairs of nitrogen atoms from NO$_2$ groups.

The activation barrier of a competing nitro-nitrite rearrangement (**TS$_2$**, Figure 1) is almost 12 kcal/mol lower than the •**R1** + •NO$_2$ radical asymptote (Figure 1). Note that the geometry of the three-center **TS$_2$** (Supporting Information, Section 7) is reminiscent of the "tight" transition states recently reported for nitroalkyl radicals.[52,53] It is also worth mentioning that the computed energetics of **TS$_2$** also agrees well (within 1 kcal/mol) with the DFT results reported before.[25] The product of this reaction, nitrite **2**, is prone to a very fast elimination of •NO radical (Figure 1, left side). The activation barrier of this process ($\Delta H^{\ddagger}$ = 2.6 kcal/mol, Figure 1) corresponds to a picosecond lifetime of **2** at room temperature. Taking into account the close coincidence between the DFT calculated activation barrier and the widely cited experimental activation energy of ~58 kcal/mol,[23] Huang et al.[25] speculated the nitrite isomerization to be the primary reaction of **1** thermolysis.

Intramolecular isomerization of **1** to aci-form **3** occurs via **TS$_{3a}$** (Figure 1, right side). Compound **3** undergoes subsequent cyclization to a substituted dihydrofurazan **I$_{3b}$** followed by water elimination yielding aminonitrofurazane **P3** (Figure 1, right side). The activation energy of the whole process can be estimated as ~67 kcal/mol (Figure 1). On the basis of DFT calculated *thermodynamics* of processes (1)−(3), Dorsett[35] proposed the process (3) leading to water elimination to be the feasible primary reaction of DADNE thermolysis. However, this process should be discarded on kinetic grounds. It is also worth mentioning that the PES region relevant to the **1** → **3** isomerization has a complicated topology. This issue is discussed in detail in the Supporting Information (Section 1).

However, the most striking result of the present contribution is that *none* of previously discussed conventional reactions dominate the gas phase thermolysis of DADNE. On the

Scheme 3. Kinetic Scheme of the Intramolecular Cyclization of DADNE Followed by Molecular Decomposition (Pathway 5)[a]
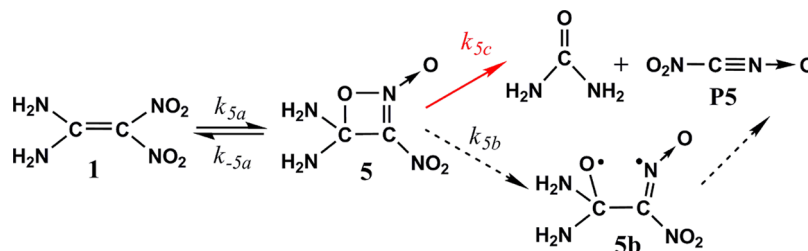
[a]The rate-limiting stage is marked in red.

Table 1. Activation Enthalpies ($\Delta^{\ddagger}H°$) and Gibbs Free Energies ($\Delta^{\ddagger}G°$) at 298 K along with the Arrhenius Parameters (Preexponential Factors A and Activation Energies E_a)[a] **Corresponding to the Rate Constants of the Gas Phase Decomposition Reactions of DADNE (1−5)**[b]

reaction		$\Delta^{\ddagger}H°$, kcal/mol	$\Delta^{\ddagger}G°$, kcal/mol	$\log(A/\text{s}^{-1})$	E_a, kcal/mol
DADNE → $^{\bullet}$R1 + $^{\bullet}$NO$_2$	(k_1)	(73.2)[c]	(58.2)[c]	18.00[d]	73.0[e]
DADNE → 2	(k_2)	60.2	60.2	13.71	61.1
DADNE → P3 + H$_2$O	($k_{3\text{eff}}$)	67.2	68.4	12.69	67.9
DADNE → 4	(k_{4a})	**48.4**	**47.6**	**14.15**	**49.1**
DADNE → 5	(k_{5a})	28.7	28.4	13.80	29.4
5 → DADNE	(k_{-5a})	1.8	1.5	13.54	2.5
5 → P5 + urea	(k_{5c})	27.8	26.7	14.30	28.7
DADNE → P5 + urea	($k_{5\text{eff}}$)	**54.7**	**53.6**	**14.56**	**55.6**

[a]The details of calculations are given in the Supporting Information (section 5). [b]The reaction pathways and numeration are in accordance with Figures 1 and 2 and Schemes 1−3. [c]In the case of barrierless radical decomposition reactions, the enthalpies ($\Delta_r H°$) and Gibbs free energies ($\Delta_r G°$) of reaction at 298 K are listed in parentheses. [d]The higher estimate on the basis of experimental data (see refs 36 and 37). [e]Estimated using the transition state theory expression $E_a = \Delta_r H° + RT$.

contrary, we succeeded in revealing two new competing primary decomposition channels, which have never been discussed before (Figure 2). These new reactions are an enamine−imine isomerization (TS$_{4a}$ in Figure 2, encircled in blue) leading to a substituted dinitroalkane 4 and an intramolecular cyclization yielding a derivative of an oxazete-N-oxide 5 (TS$_{5a}$ in Figure 2).

In accordance with computational results (Figure 2) and subsequent decomposition of the dinitroalkane intermediate, 4 is the most favorable channel of DADNE decomposition. The kinetic scheme of this process (4) is shown in Scheme 2.

The limiting step of this decomposition pathway is the H-transfer reaction (TS$_{4a}$, $\Delta H^{\ddagger}$ = 48.4 kcal/mol, Figure 2) yielding 1-amino-1-imino-2,2-dinitroethane, 4 (k_{4a}, Scheme 2). The intermediate 4 may decompose either by molecular mechanism (k_{4m}, Scheme 2; TS$_{4m}$, Figure 2) leading to cyanamide and aci-dinitromethane P4 or by radical mechanism leading to $^{\bullet}$NO$_2$ and $^{\bullet}$R4 radicals (k_{4r}, Scheme 2; TS$_{4r}$, Figure 2). Note that the endothermicity of the latter reaction (4r) is 41.8 kcal/mol (cf. 72.0 kcal/mol in the case of 1 → $^{\bullet}$R1 + $^{\bullet}$NO$_2$, Figure 1).[54] The activation barrier of the competing molecular decomposition (4m) is slightly lower, viz., $\Delta H^{\ddagger}$ = 39.4 kcal/mol (Figure 2). Given the fact that the typical preexponental factors corresponding to C−NO$_2$ homolytic bond cleavage in dinitroalkanes ($\log A \approx 15-16$)[37] are 2−3 orders of magnitude higher than the normal one ($\log A \approx 13$), the reaction (4r) might be faster than (4m) even at room temperature. In the present case, the former reaction channel yields $^{\bullet}$NO$_2$ radical through the intermediacy of 4, while the kinetic parameters correspond to a limiting stage (TS$_{4a}$) with a normal preexponential factor.

The kinetic scheme of the competing decomposition channel (5) is shown in Scheme 3. This reaction proceeds via the intramolecular cyclization yielding a four-membered substituted heterocycle, viz., oxazete-N-oxide 5 (Scheme 3, Figure 2). The heterocycle 5 may decompose via the concerted molecular mechanism (k_{5c}, Scheme 3; TS$_{5c}$, Figure 2) leading to urea and intermediate P5.

However, the same products may be formed in a sequence of transformations accompanying the ring opening of 5 (k_{5b}, Scheme 3, Figure S3 of the Supporting Information). Thermodynamics of the stationary points on the PES for this channel have only been estimated at the DFT level using the broken symmetry approach for the singlet open-shell species (e.g., a biradical 5b, Scheme 3). According to these calculations, the probabilities of product formation through both channels are similar (see section 2 and Figure S3 of the Supporting Information). Nevertheless, more accurate multireference calculations are indeed desirable to clarify this issue. Note that a similar mechanism was also proposed in the case of nitroethylene.[55]

In contrast to the process (4), the barrier of a reverse reaction 5 → 1 is very low (1.7 kcal/mol, Figure 2), and the reversion of 5 to the starting compound (k_{-5a}, Scheme 3) is significantly faster than its decay ($k_{-5a} \gg k_{5c}$). Therefore, the effective rate constant of 1 decomposition through the intermediacy of 5 can be estimated as $k_{5\text{eff}} \approx ((k_{5a})/(k_{-5a}))k_{5c}$ with the activation energy of the overall decomposition process being ~56 kcal/mol.

Thus, according to our high-level calculations (Figures 1 and 2), reaction (4) is the most favorable channel of DADNE decomposition. The reason for this preference is a push−pull nature of its electronic structure, which facilitates the H-transfer reaction (4a, Figure 2, Scheme 2). To validate this assertion, we performed calculations for a DADNE isomer lacking the push−pull nature, viz., 1,2-diamino-1,2-dinitroethylene (iso-DADNE).

In the case of iso-DADNE, the H atom migration turned out to be *the least favorable* kinetically among the counterparts of (1)−(5) reactions (Figure S4 and section 3 of the Supporting Information).

For clarity, we summarized the most important findings in Table 1. Apart from activation enthalpies and Gibbs free energies (Figures 1 and 2), we calculated the Arrhenius parameters of the elementary rate constants for all channels (1−5) in the temperature range of 400−550 K using the transition state theory. Details of the calculations are given in the Supporting Information (section 5 and Table S2). We also represented the temperature dependences of all rate constants in Figure 3. Although reaction (4) has the lowest activation
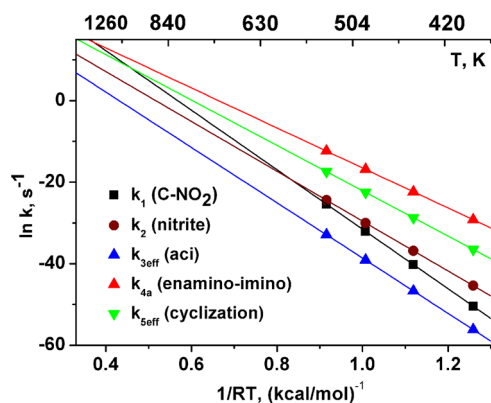

Figure 3. Rate constants in the Arrhenius coordinates for the gas phase decomposition reactions of DADNE (1−5).

energy in the case of DADNE decomposition, the C−NO$_2$ bond fission (1) has indeed a much higher preexponential factor A. Thus, the latter reaction should dominate at high enough temperatures. Assuming the higher estimate[36,37] of the ratio A_1/A_{4a} to be 10^4 and the difference in activation energies ∼24 kcal/mol (Figures 1 and 2), the isokinetic temperature for processes (1) and (4) should be higher than 1000 °C (Figure 3). All previously discussed experiments[23,24,29−31] were performed at temperatures below 300 °C. Thus, the H atom migration followed by decomposition of the dinitroalkane intermediate **4** is the most feasible primary reaction of DADNE thermolysis at least in the gas phase at temperatures below 1000 °C.

However, it is obvious that the conclusions inferred from modeling the gas phase processes cannot be simply extended to real solid materials. It is well-known that the DADNE molecules in a crystal are packed in infinite twisted two-dimensional (2D) layers with an extensive network of intra- and intermolecular hydrogen bonds.[26,56] Nevertheless, despite the presence of two strong intramolecular H-bonds (the DFT calculated H···O distance is ∼1.85 A), the previously discussed push−pull nature of the DADNE electronic structure renders the rotational barrier of C(NH$_2$)$_2$ moiety around the double bond (DFT and CASSCF estimations) to be quite low (∼17 kcal/mol; cf. ∼65 kcal/mol in the case of ethylene).[57] It is therefore reasonable to expect much weaker intermolecular H-bonds (the closest H···O distance is ∼2.2 A)[56] not to affect the activation barriers strongly.

Moreover, the account of the crystalline environment and, furthermore, defects, mechanical strain, and so on, can significantly affect rate constants and activation energies of competing reactions and even change their relative impor-

tance.[34,40] More specifically, the solid state DFT calculations revealed a huge increase (by ∼20 kcal/mol) in the activation energy of the C−NO$_2$ bond fission in a defect-free crystal,[34] while the shear−strain deformations lead to tremendous decrease in the activation energy.[40] In contrast, the barrier of the nitro-nitrite rearrangement was reduced by ∼20 kcal/mol in the ideal crystal and was almost insensitive to the shear−strain deformations.[40] In the case of newly proposed pathways (4) and (5), it is reasonable to expect the first stages (4a) and (5a) with a moderate activation volume to be less affected by environment, while the subsequent reactions (4r) and (5c) might be hindered to some extent. More detailed studies are necessary to clarify this issue.

■ CONCLUSION

On the basis of previously discussed computational results, the following remarks on the mechanism of the DADNE thermal decomposition can be made. In contrast to the case of nitroalkenes and nitroaromatics, the particular chemical structure of DADNE (nitro−enamino) favors two decomposition channels never discussed before. The most favorable gas phase reaction is the enamine−imino isomerization (4a) with the activation energy of ∼49 kcal/mol (Table 1) followed by either radical (4r) or molecular (4m) decomposition of the dinitroalkane intermediate **4** (Scheme 2, Figure 2). The closest competing process (the activation energy of ∼56 kcal/mol, Table 1) is the reversible intramolecular cyclization (5a) with a subsequent concerted decomposition (5c) yielding urea and the intermediate **P5** (Scheme 3, Figure 2). The rate constant estimations show that the former decomposition channel dominates over C−NO$_2$ bond fission at the temperatures below 1000 °C (Figure 3).

More generally, the considered pathways (4) and (5) can also be relevant for a wide series of unsaturated hydrocarbons substituted with both nitro- and amino-groups. E.g., in the case of triaminotrinitrobenzene (TATB), the DFT estimations give evidence that the activation barriers of the latter decomposition pathways and nitro−nitrite rearrangement are very close to each other (Figure S7, section 6, of the Supporting Information).

This issue clearly points out that the initiation chemistry, even in the case of relatively simple compounds such as DADNE, should not be reduced (as often happens) to a "rupture of the weakest bond". Chemical transformations mediated by the intermediacy of transient species (e.g., in the case of **5**, unfavorable both thermodynamically and kinetically; cf. Figure 2) can render viable entirely unexpected reactions. We have already faced similar issues dealing with the decomposition of tetrazole derivatives.[58,59] Attention should always be paid to thorough consideration of feasible primary reaction channels and equilibria with short-lived intermediates.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text describing PES regions relevant to nitro−aci nitro isomerization of DADNE and prototypical systems, to decomposition of the biradicoloid intermediate, to decomposition of the DADNE isomer, and to decomposition of the triaminotrinitrobenzene and benchmark computations of various multilevel and post-Hartree−Fock procedures, figures showing relative enthalpies, potential energy profiles, Arrhenius rate constants, and thermal decomposition channels, tables listing activation enthalpies of polynitoralkane thermal

reactions, activation enthalpies, Gibbs free energies, and Arrhenius parameters of DADNE decomposition reactions, reagents and intermediates and their optimized geometries and thermal corrections to thermodynamic potentials of all compounds under study. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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