

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/263948583>

Surface-Accelerated Decomposition of δ -HMX

ARTICLE in JOURNAL OF PHYSICAL CHEMISTRY LETTERS · FEBRUARY 2013

Impact Factor: 7.46 · DOI: 10.1021/jz302166p

CITATIONS

17

READS

29

3 AUTHORS:



[Onise Sharia](#)

University of Notre Dame

35 PUBLICATIONS 372 CITATIONS

SEE PROFILE



[Roman Tsyshevskiy](#)

University of Maryland, College Park

25 PUBLICATIONS 91 CITATIONS

SEE PROFILE



[Maija M. Kuklja](#)

University of Maryland, College Park

115 PUBLICATIONS 1,671 CITATIONS

SEE PROFILE

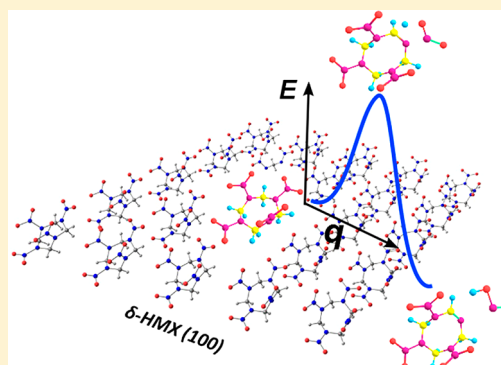
Surface-Accelerated Decomposition of δ -HMX

Onise Sharia, Roman Tsyshevsky, and Maija M. Kuklja*

Materials Science and Engineering Department, University of Maryland, College Park, Maryland 20742, United States

ABSTRACT: Despite extensive efforts to study the explosive decomposition of HMX, a cyclic nitramine widely used as a solid fuel, explosive, and propellant, an understanding of the physicochemical processes, governing the sensitivity of condensed HMX to detonation initiation is not yet achieved. Experimental and theoretical explorations of the initiation of chemistry are equally challenging because of many complex parallel processes, including the β - δ phase transition and the decomposition from both phases. Among four known polymorphs, HMX is produced in the most stable β -phase, which transforms into the most reactive δ -phase under heat or pressure. In this study, the homolytic NO_2 loss and HONO elimination precursor reactions of the gas-phase, ideal crystal, and the (100) surface of δ -HMX are explored by first principles modeling. Our calculations revealed that the high sensitivity of δ -HMX is attributed to interactions of surfaces and molecular dipole moments. While both decomposition reactions coexist, the exothermic HONO-isomer formation catalyzes the N-NO_2 homolysis, leading to fast violent explosions.

SECTION: Surfaces, Interfaces, Porous Materials, and Catalysis



Cyclotetramethylene-tetranitramine (HMX), an important energetic material, has four known crystalline phases labeled α , β , γ , and δ , with different propensities to initiate explosive decomposition reactions,¹ referred to as sensitivity. Understanding sensitivity of energetic materials to detonation initiation is one of the stubborn challenges in the field of matter under extreme conditions that hamper progress in science and technology and prevent a full utilization of an enormous potential of high energy density materials. In addition to unresolved fundamental problems with the initiation of chemistry and the energy release mechanisms, the explosive materials often ignite too easily or accidentally and pose danger during storage, handling, and transportation. With many factors suggested to contribute to the sensitivity of energetic materials (density, hot spots, voids, cracks, shear-strain deformations, electronic excitations, and particle sizes), the full picture of rapid explosive decomposition reactions is as complex as far from completion.

Among four HMX polymorphs, the β -phase, the form in which HMX is normally produced, has the highest density and is stable at room temperature.² When heated to temperatures above 435 K, the monoclinic β -phase converts to the hexagonal δ -HMX,³ the most reactive phase.^{1,4} The transformation involves major changes of both the HMX crystal lattice and the molecular ring conformation from β (chair) to δ (boat)^{1,3,4} (Figure 1). With many experimental reports declaring a high sensitivity of the δ -phase, atomistic theoretical investigations are scarce,^{5–7} and the detailed reasons behind the HMX behavior remain puzzling. The situation is further complicated by the fact that the decomposition of the δ -phase practically coincides with the β -to- δ phase transition and the possible decomposition of the β -phase. It was speculated that the

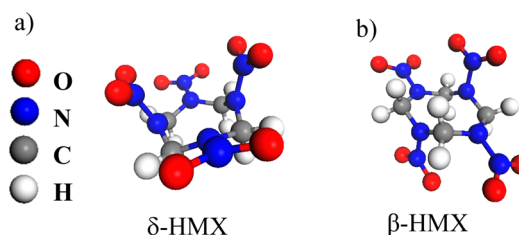


Figure 1. Molecular structures of (a) δ - and (b) β -HMX. In the β -phase lattice, each $\text{H}_8\text{C}_4\text{N}_8\text{O}_8$ molecule has a chair conformation in which two NO_2 groups are on one side of the C_4N_4 ring and the other two NO_2 groups are on the opposite side of the ring. Each molecule in the δ -phase is in the boat conformation, having all four NO_2 groups on the same side of the C_4N_4 ring.

observed sensitivity increase of the δ -phase^{3,8} is due to a significant lattice expansion and the associated density decrease from 1.90 for β to 1.78 g/cm^3 for δ , accompanying the β -to- δ phase transition,⁹ which results in an appearance of cracks, large amount of hot spots in the material, and the fast growth of reaction during shock compression.⁸ Naturally, the available experimental techniques measure only global kinetics^{8,10} and do not distinguish between the individual processes that have very close activation barriers. Hence atomistic details of the δ -HMX phase decomposition mechanisms and kinetics are yet to be established.

In this Letter aimed at gaining a better understanding of materials factors that control sensitivity in HMX, we explore

Received: December 28, 2012

Accepted: February 8, 2013

Published: February 8, 2013

earliest decomposition reactions in the δ -phase HMX by means of density functional theory (DFT) combined with transition-state theory (TST) and propose a mechanistic explanation of its increased sensitivity. The N–NO₂ homolysis and concerted HONO elimination precursor reactions are simulated for an isolated δ -HMX molecule, the molecule placed in the ideal crystal, and that on a free surface. A comparison with the previously obtained results for β -HMX¹¹ suggests reasons that make δ -HMX so much more sensitive. First, activation barriers of the surface reactions significantly drop, and the corresponding reaction rates appreciably accelerate. Second, the HONO-isomer formation mechanism in δ -HMX becomes exothermic due to interactions between a molecular dipole moment and the crystal surface, and the resultant reaction heat is used by the system for further rapid decomposition and the propagation of the reaction.

The calculations are performed within DFT^{12,13} in the GGA approximation with the PBE exchange–correlation functional¹⁴ and PAW pseudopotentials¹⁵ as implemented in the plane wave code VASP.¹⁶ The kinetic energy cutoff was set to 600 eV. The structure of the gas-phase and solid-phase molecule agrees well with earlier experimental and theoretical studies.¹⁷ In simulating an ideal δ -HMX crystal with the $P6_1$ symmetry,³ the theoretical lattice constants of the hexagonal unit cell consisting of 168 atoms are calculated as $a_0 = 8.180$ and $c_0 = 33.152$ Å, which compare to experimental values³ of 7.711 and 32.553 Å within a typical accuracy of the GGA-PBE functional. In calculations, the $2 \times 2 \times 1$ k -point mesh was used for the unit cell of ideal δ -HMX, and the reduced number of k -points was used for larger supercells to keep the k -point density consistent.

Gas-phase decomposition reactions were modeled by placing a single δ -HMX molecule in $15 \times 15 \times 15$ Å³ periodic box and relaxing all atomic coordinates. The calculations were performed at Γ k -point only. The results of the gas-phase decomposition were additionally validated with test calculations carried out by molecular code Gaussian with the PBE functional and the 6-31+G(2df, p) basis set. The supercell for modeling bulk reactions ($a = 16.36$, $b = 14.168$, $c = 33.152$ Å, $\alpha = \beta = \gamma = 90^\circ$) was constructed by choosing modified lattice vectors, $\vec{a} = 2(\vec{a}_0 + \vec{b}_0)$, $\vec{b} = -\vec{a}_0 + \vec{b}_0$, and $\vec{c} = \vec{c}_0$ shown in Figure 2a. Surface reactions were simulated by using a slab model consisting of the (100) four-molecule-thick surface layer on top of 10 Å of vacuum (Figure 2b). The large size of the supercells ensured that spurious interactions between reactants and reaction products in neighboring cells were minimal.

All atomic positions were relaxed using the quasi-Newton and conjugate gradient methods. Minimal energy paths were obtained with the nudged elastic band method.¹⁸ Reaction rates were calculated by applying TST¹⁹ for reactions with well-defined transition states and variational TST²⁰ for reactions with no barriers, as described elsewhere.¹¹

The homolytic cleavage of a N–NO₂ bond is assumed to be the most favorable primary decomposition channel of nitramines. The obtained activation barriers collected in Table 1 indicate that the dissociation energies of axial and equatorial nitro groups in the gas-phase δ -HMX molecule are almost the same (44.8 kcal/mol) and slightly higher than the energy of NO₂ loss in β -HMX (42.8 and 44.6 kcal/mol for axial and equatorial groups, respectively),¹¹ in agreement with earlier calculations (~ 45.5 kcal/mol).⁶

The concerted elimination of nitrous acid from HMX is usually considered as a competing with the N–NO₂ homolysis

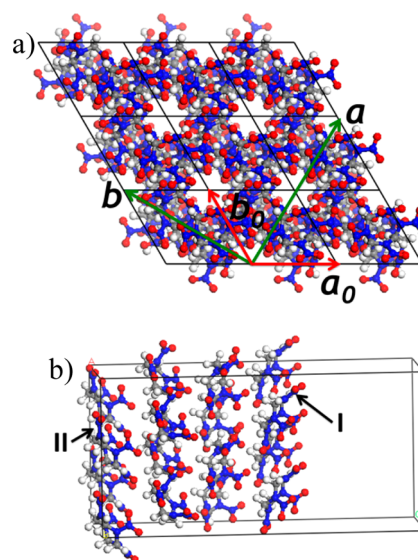


Figure 2. (a) The crystal structure of δ -HMX is shown in projection onto a (110) surface, with modified, a , b , and original, a_0 , b_0 lattice vectors. (b) The slab model shows the nonidentical configurations of HMX molecules (I) and (II) with respect to the (100) surface.

channel due to a relatively low activation energy. The calculated activation barrier of the HONO elimination (37.8 kcal/mol) is more than 7 kcal/mol lower than the energy of the homolytic NO₂ loss (Table 1). This is in contrast with earlier calculations reported for the HONO activation barrier (50.6 kcal/mol), which is ~ 5 kcal/mol higher than the energy of N–NO₂ bond cleavage.⁶ The difference stems from different DFT functionals, PBE used in this study versus B3LYP used in ref 6. Nevertheless, a comparison of the reaction rates (Figure 3a) and pre-exponential factors (Table 1) shows that the NO₂ loss proceeds with a higher rate than the HONO elimination.

Although the activation barrier for the HONO pathway of δ -HMX is slightly lower than of the β -conformer (43.3 kcal/mol)¹¹ and the reaction is slightly exothermic (-2.2 kcal/mol, Table 1), the difference is too small to account for the significant change in sensitivity of β - and δ -phases. Hence, the modification of the molecular conformation from β (chair) to δ (boat) configuration makes, at best, only a minor contribution toward increasing sensitivity of the δ -phase. We also note that the results obtained using periodic VASP code are in good agreement with those produced from gas-phase calculations employing molecular Gaussian code (Table 1), which additionally confirms the drawn conclusion.

Modeling of the solid-state decomposition reactions is especially complex due to molecular interactions⁴ with the crystalline field and a manifold of local minima on the potential energy surface.²¹ The detachment of NO₂ in bulk δ -HMX requires an energy of ~ 50.8 kcal/mol, which is ~ 5 kcal/mol higher than that in the gas phase (Table 1). The activation barrier for the HONO pathway, 49.4 kcal/mol, is ~ 12 kcal/mol higher than that in the isolated molecule. Both reactions have similar energies, implying that they would start at approximately the same temperatures and would likely compete. Comparing the obtained energetics, we note that the decomposition scenarios in the ideal crystals of both β - and δ -HMX are very similar, with fairly high activation barriers of 47.9–52.7 kcal/mol for the N–NO₂ split and HONO elimination in β -HMX and 49.4–50.8 kcal/mol for the

Table 1. Energetic and Kinetic Parameters of δ -HMX Decomposition Reactions

| | gas phase | | solid-state phase | |
|---|---|--------------------------|--|--------------|
| | N-NO ₂ | HONO | N-NO ₂ | HONO |
| reaction energy (kcal/mol) | (ax) 44.8 (45.1) ^a (eq) 44.8 (46.3) | -2.2 (-2.4) ^b | (I) 39.9 ^c [50.8] ^d (II) 34.1 | -32.0 [-2.8] |
| activation barrier (kcal/mol) | (ax) 44.8 (45.1) (eq) 44.8 (46.3) | 39.2 (38.0) | (I) 39.9 [50.8] (II) 34.1 | 25.6 [49.4] |
| ZPE corrected activation barrier (kcal/mol) | (ax) 39.2 (40.3) (eq) 40.0 (42.0) | 32.9 (33.3) | (I) 34.3 (II) 30.1 | 22.8 |
| log A (1/s) | 18 | 14 | 18 | 13 |

^aThe energies in parentheses, obtained from Gaussian calculations, are given here for comparison. ^bA negative energy corresponds to an exothermic reaction. ^cThe (100) surface of δ -HMX. ^dThe ideal bulk δ -HMX crystal.

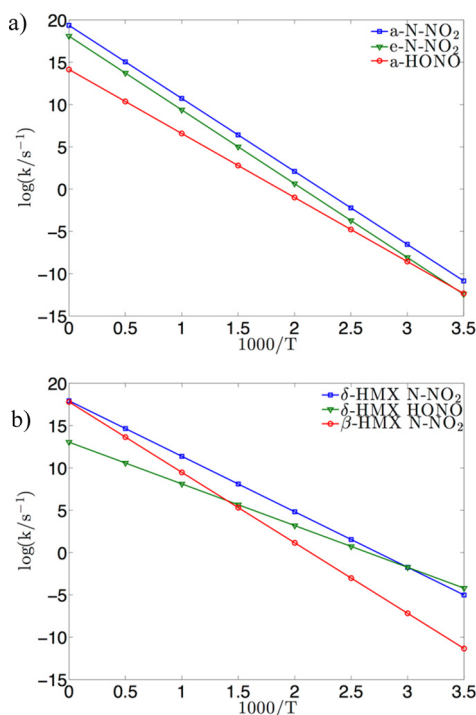


Figure 3. Reaction rates for the NO₂ loss and HONO elimination channels of HMX (a) in the gas phase and (b) at the (100) surface of β - and δ -HMX.

corresponding reactions in δ -HMX. The observed difference is small (~ 1 – 2 kcal/mol), and although the HONO elimination in δ -HMX shows some exothermicity (-2.8 kcal/mol), the change of both the molecular conformation and the crystalline arrangement in the ideal (defect-free) materials faces difficulties in offering a clear and simple explanation of a major sensitivity change from one solid phase to another.

Further, we will explore the surface decomposition and demonstrate that the surface-induced effect on the decomposition kinetics of δ -HMX has dramatic consequences. We selected the (100) surface out of many possible HMX surfaces because it provides an opportunity to investigate both equatorial and axial N-NO₂ homolysis reactions of δ -HMX. Figure 2b shows the nonidentical configurations (I) and (II) of the HMX molecule relative to the free surface. Due to the particular molecular arrangement in δ -HMX, the molecular configuration (I) allows one to study both equatorial and axial nitro group decompositions on the (100) surface. In the configuration (II), the molecule is positioned in such a way that only axial NO₂ groups are exposed to a surface effect, while

equatorial groups are expected to behave similarly to bulk molecules due to their local neighbor surroundings.

Among the possible N-NO₂ homolysis reactions probed, the lowest activation energy (34.1 kcal/mol) corresponds to the axial N-NO₂ bond cleavage (configuration II, Figure 2b); this is ~ 10 kcal/mol lower than the similar reaction required in the gas phase and ~ 15 kcal/mol lower than the ideal bulk reaction (Table 1). The obtained activation barrier is in agreement with that from experiment (34.4 kcal/mol).¹⁰

The activation barrier of the axial HONO elimination is 25.6 kcal/mol; the obtained decreases of almost 15 kcal/mol in comparison to that in the gas phase and 25 kcal/mol in comparison to that in the bulk are rather significant. Plotted reaction rates versus reciprocal temperature (Figure 3b) demonstrate that the HONO is the predominant decomposition channel in the low-temperature range (up to ~ 330 K),²² whereas at higher temperatures, the NO₂ loss possesses higher rates due to the noticeably large pre-exponential factor (Table 1, Figure 3b). The calculated reaction constants (log A) of 13–17 1/s are in reasonable agreement with the experimental value of 15.3.¹⁰ Finally, in addition to having the low activation barrier, the surface HONO formation is a highly exothermic reaction, releasing 32.0 kcal/mol, while the reactions in the gas-phase and bulk δ -HMX proceed with a negligible exothermicity. As seen from Table 1, the amount of heat released in the course of the reaction is sufficient to trigger the next HONO elimination and the axial N-NO₂ bond rupture. Thus, for δ -HMX molecules that are situated on the (100) surface, the chemistry will develop violently due to very initial reactions being exothermic.

Summing up, the initial decomposition mechanisms in δ -HMX, the N-NO₂ homolysis and HONO reactions, which are typical explosive initiation reactions in nitro compounds, were explored by means of DFT in combination with variational TST. The activation barriers, pre-exponential factors, and reaction rates were obtained as a function of the molecular environment for the decomposing molecules placed in the gas phase, in the ideal bulk crystal, and on the (100) crystal surfaces. The calculated energetic and kinetic parameters were analyzed and compared for β - and δ -HMX polymorphs to better understand much higher sensitivity to initiation of detonation of the solid δ -phase versus β -phase.

We found that the change of the HMX molecular conformation from β (chair, C_i symmetry) to δ (boat, C_{2v} symmetry) configuration does not cause significant changes in the decomposition pathways or their kinetics. The dissociation barrier for NO₂ splitting off in the gas-phase δ -HMX molecule is slightly higher than that in β -HMX, and the activation barrier for the HONO pathway is somewhat lower (by ~ 6 kcal/mol)

than that in the β -conformer. The most noticeable change is some dominance of the weakly exothermic HONO channel over the endothermic N–NO₂ homolysis in the δ -HMX molecule, while in the β -HMX molecule, those pathways are endothermic with the close activation energies. The similar situation is observed for the ideal (defect-free) crystals. The change of the crystalline arrangement from the β -HMX phase ($P2_1$ space group) to the δ -HMX phase ($P6_1$ space group) does not induce significant differences in the decomposition chemistry. The derived activation barriers of the HONO elimination and the N–NO₂ split (49.4–50.8 kcal/mol) in δ -HMX are comparable to the corresponding reactions (47.9–52.7 kcal/mol) in β -HMX. The observed difference is small (~ 1 –2 kcal/mol), and the HONO formation in δ -HMX remains weakly exothermic (-2.8 kcal/mol).

A disparity between the densely packed β - and the lower-density δ -HMX structures is manifested in the presence of channels piercing the δ -HMX crystal (Figure 2a). Connecting the large activation volume required for the N–NO₂ reaction to occur with the generous empty space available in the δ -HMX crystal raises an argument in favor of the reduced barriers and/or accelerated kinetics for reactions proceeding along those passages. Our simulations however fall short in supporting this possibility. Placing the NO₂ moiety in the middle of the crystal passage results in neither the lower activation barrier nor faster reaction rate. Therefore, the lower density of the δ -phase and even the presence of the spacious empty channels in the crystal lattice do not produce any favorable conditions for the accelerated chemistry or higher sensitivity of δ -HMX. Indeed, neither the change of the molecular conformation nor the crystalline arrangement in the defect-free materials offers an explanation of a major sensitivity change from one HMX solid phase to another.

Previously, we discovered that the crystal arrangement significantly increases activation barriers or even suppresses some decomposition channels,^{11,23} while surfaces and interfaces²⁴ reduce the activation barriers for the N–NO₂ homolysis in RDX²⁵ and β -HMX.¹¹ Evidently, the surface-induced effect happened to be much more pronounced in δ -HMX. While the activation barrier for the surface decomposition drops ~ 4 –8 kcal/mol in β -HMX (compare to bulk), in δ -HMX, it decreases ~ 10 –25 kcal/mol. The most significant reduction of nearly 50% is observed for one of the surface HONO reactions, for which the activation barrier becomes as low as 25.6 kcal/mol (22.8 kcal/mol with ZPE correction; Table 1). The barrier reduction in β -HMX has been attributed to missing interactions of surface molecules with their neighbors (in comparison to bulk), which causes 0.02–0.04 Å elongation of N–NO₂ bonds.¹¹ Unlike β -HMX, the geometry of the surface molecule does not change much in the δ -phase.

We suggest that the reduction of the activation barrier, which is tightly coupled with the change of the endothermic to exothermic decomposition chemistry in the δ -phase, is due to the polar nature of the (100) surface. Dependence of the chemical reactivity on the direction of a polar axis in polar organic crystals was discussed; for example, in ref 26, it was argued that initiation of the reaction may be favored at a single side of the crystal and that the polar axis of the crystal directs the reaction. Speculating along those lines, we propose that the interaction between the dipole moment of the δ -HMX molecule and the polar (100) surface that induces an electronic density redistribution in the material is responsible for such a striking difference in the decomposition chemistry of δ -HMX.

The most important consequence is that the HONO formation becomes exothermic on the surface, releasing ~ 32 kcal/mol, sufficiently large energy to trigger the following dissociation act. The key here is that while the N–NO₂ homolysis and the HONO elimination precursor reactions coexist in δ -HMX decomposition, the role of HONO-isomer is autocatalytic, and that is what determines such a high sensitivity of the δ -phase.

AUTHOR INFORMATION

Corresponding Author

*E-mail: mkukla@nsf.gov, mkukla@umd.edu.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This research is supported in part by ONR (Grant N00014-12-1-0529) and NSF. We used NSF XSEDE resources (Grant DMR-100054) and DOE NERSC resources (Contract DE-AC02-05CH11231). M.M.K. is grateful to the Office of the Director of NSF for support under the IRD program. Any appearance of findings, conclusions, or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of NSF.

REFERENCES

- (1) Brill, T. B.; Reese, C. O. *J. Phys. Chem.* **1980**, *84*, 1376–1380.
- (2) Choi, C. S.; Boutin, H. P. *Acta Crystallogr., Sect. B* **1970**, *26*, 1235–1240.
- (3) (a) Cady, H. H.; Larson, A. C.; Cromer, D. T. *Acta Crystallogr., Sect. B* **1963**, *16*, 617. (b) Cobbleddick, R. E.; Small, R. W. H. *Acta Crystallogr., Sect. B* **1974**, *30*, 1918–1922. (c) Herrmann, M.; Engel, W.; Eisenreich, N. Z. *Kristallogr.* **1993**, *204*, 129–142.
- (4) Brill, T. B.; Karpowicz, R. J. *J. Phys. Chem.* **1982**, *86*, 4260–4265.
- (5) Lewis, J. P. *Chem. Phys. Lett.* **2003**, *371*, 588–593.
- (6) Chakraborty, D.; Muller, R. P.; Dasgupta, S.; Goddard, W. A., III. *J. Phys. Chem. A* **2001**, *105*, 1302–1314.
- (7) Manaa, M. R.; Fried, L. E.; Melius, C. F.; Elstner, M.; Frauenheim, Th. *J. Phys. Chem. A* **2002**, *106*, 9024–9029.
- (8) Urtiew, P. A.; Forbes, J. W.; Tarver, C. M.; Vandersall, K. S.; Garcia, F.; Greenwood, D. W.; Hsu, P. C.; Maienschein, J. L. *AIP Conf. Proc.* **2004**, *706*, 1053–1056.
- (9) Henson, B. F.; Asay, B. W.; Sander, R. K.; Son, S. F.; Robinson, J. M.; Dickson, P. M. *Phys. Rev. Lett.* **1999**, *82*, 1213–1216.
- (10) (a) Whelan, D. J.; Fitzgerald, M. R. *A Reassessment of the Kinetics of the Thermal Decomposition of the High Explosive, Delta-HMX, in the Range 508 to 524 K, as Studied by Isothermal Gravimetry*; NASA: Melbourne, 1998 (b) Bulusu, S.; Weinstein, D. I.; Autera, J. R.; Velicky, R. W. *J. Phys. Chem.* **1986**, *90*, 4121–4126.
- (11) (a) Sharia, O.; Kuklja, M. M. *J. Phys. Chem. A* **2010**, *114*, 12656–12661. (b) Sharia, O.; Kuklja, M. M. *J. Phys. Chem. B* **2011**, *115*, 12677–12686. (c) Sharia, O.; Kuklja, M. M. *J. Phys. Chem. C* **2012**, *116*, 11077–11081. (d) Sharia, O.; Kuklja, M. M. *J. Am. Chem. Soc.* **2012**, *134*, 11815–11820.
- (12) Hohenberg, P.; Kohn, W. *Phys. Rev.* **1964**, *136*, B864–B871.
- (13) Kohn, W.; Sham, L. J. *Phys. Rev. A* **1965**, *140*, A1133–A1138.
- (14) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
- (15) Blöchl, P. E. *Phys. Rev. B* **1994**, *50*, 17953–17979.
- (16) (a) Kresese, G.; Futhmuller, J. *Comput. Mater. Sci.* **1996**, *6*, 15–50. (b) Kresese, G.; Furthmuller, F. *Phys. Rev. B* **1996**, *54*, 11169–11186. (c) Kresese, G.; Hafner, J. *Phys. Rev. B* **1993**, *47*, RC558–561.
- (17) Brand, H. V.; Rabie, R. L.; Funk, D. J.; Diaz-Acosta, I.; Pulay, P.; Lippert, T. K. *J. Phys. Chem. B* **2002**, *106*, 10594–10604.
- (18) Henkelman, G.; Uberuaga, B. P.; Jónsson, H. *J. Chem. Phys.* **2000**, *113*, 9901–9904.

- (19) Hanggi, P.; Talkner, P.; Borkovec, M. *Rev. Mod. Phys.* **1990**, *62*, 251–341.
- (20) Garrett, B. C.; Truhlar, D. G. *J. Phys. Chem.* **1979**, *83*, 1052–1079.
- (21) (a) Zerilli, F. J.; Kuklja, M. M. *J. Phys. Chem. A* **2010**, *114*, 5372–5376. (b) Zerilli, F. J.; Kuklja, M. M. *J. Phys. Chem. A* **2006**, *110*, 5173–5179.
- (22) The critical temperature at which dominating decomposition mechanisms switch can be only approximately determined from first-principle calculations and should not be regarded as precisely predicted because in the model calculations (a) an entropy contribution is only partly included, (b) only the earliest initiation reactions are simulated, (c) small inaccuracies in activation barriers lead to large variations in reaction rates, and (d) taking into account the HONO reaction exothermicity, autocatalysis, various defects beyond surfaces, and other effects would change the crossing T of the competing reactions.
- (23) (a) Kuklja, M. M.; Rashkeev, S. N. *Phys. Rev. B* **2007**, *75*, 104111. (b) Kimmel, A. V.; Sushko, P. V.; Shluger, A. L.; Kuklja, M. M. *J. Phys. Chem. A* **2008**, *112*, 4496–4450.
- (24) (a) Kuklja, M. M.; Rashkeev, S. N. *Appl. Phys. Lett.* **2007**, *90*, 151913. (b) Kuklja, M. M.; Rashkeev, S. N. *J. Phys. Chem. C* **2009**, *113*, 17–20. (c) Kuklja, M. M.; Rashkeev, S. N. *J. Phys. Chem. Lett.* **2010**, *1*, 363–367.
- (25) Kuklja, M. M. *J. Phys. Chem. B* **2001**, *105*, 10159–10162.
- (26) Curtin, D. Y.; Paul, I. C. *Chem. Rev.* **1981**, *81*, 528–541.