

Abstract Submitted  
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**A DFT and *Ab Initio* Study of the Thermal Decomposition of 1,3,3-Trinitroazetidine (TNAZ)** JEFFREY VEALS, DONALD THOMPSON, University of Missouri-Columbia — Density functional theory (DFT) and *ab initio* methods are employed to investigate unimolecular decomposition pathways of 1,3,3-trinitroazetidine (TNAZ) initiated by loss of NO<sub>2</sub> or HONO. Geometry optimizations are performed using M06/cc-pVTZ for all species commonly included in the initial decomposition mechanisms. Coupled-cluster (CC) theory with single, double, and perturbative triple excitations [CCSD(T)], is used to calculate more accurate single point energies at the M06/cc-pVTZ geometries. The CCSD(T)/cc-pVTZ energies for NO<sub>2</sub> elimination by N-N and C-N bond fission are 43.21 kcal/mol and 50.46 kcal/mol, respectively. The decomposition route initiated by *trans*-HONO elimination can occur by a concerted H-atom and nitramine NO<sub>2</sub> elimination or by loss of an alkyl NO<sub>2</sub> group and H-atom with energy barriers calculated using CCSD(T)/cc-pVTZ, respectively, 47.0 kcal/mol and 48.27 kcal/mol. At the CCSD(T)/cc-pVTZ level, the energy ordering of these four decomposition steps from most favored to least favored is as follows: N-N bond fission (43.21 kcal/mol), HONO elimination involving the nitramine NO<sub>2</sub> group (47.0 kcal/mol), HONO elimination involving the alkyl NO<sub>2</sub> group (48.27 kcal/mol), and finally C-N bond fission (50.46kcal/mol). Therefore the most likely initial decomposition route of TNAZ is predicted to be N-N bond fission.

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