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Cage Compounds as Potential Energetic Oxidizers: A Theoretical Study of a Cage Isomer of N_2O_3 Robert J. Buszek^[a] and Jerry A. Boatz^{*[b]}

Abstract: Ab initio electronic structure calculations are employed to investigate the cage isomer of N_2O_3 (c- N_2O_3) as a viable energetic oxidizer. c- N_2O_3 is vibrationally stable with a large heat of formation of 7.95 kJ g^{-1} and can produce larger enthalpies of combustion than other commonly used oxidizers such as ammonium perchlorate, $O_2(l)$ and N_2O_4 . c- N_2O_3 is shown to have a unimolecular decomposition barrier of 23.6 kJ mol^{-1} at the CCSD(T)/CBS(T-Q) level of theory, and a bimolecular decomposition barrier of $100.8 \text{ kJ mol}^{-1}$. Although c- N_2O_3 is predicted to perform well as an oxidizer, the low barrier to unimolecular decomposition is likely to render it impractical as an energetic oxidizer.

Keywords: Ab initio, unimolecular decomposition, cage isomer, oxidizer, enthalpy of combustion

1 Introduction

Driven by the need for better performing, low cost, and environmentally friendly propellants and explosives, the energetic materials community is constantly searching for novel species to accomplish this. Perchlorates have long been used as oxidizers by the energetic community, particularly ammonium perchlorate (AP) which has been widely used in solid rocket motors for the past 50 years. Ammonium perchlorate is stable at room temperature, decomposes at temperatures above 150°C and ignites at temperatures greater than 440°C , with an activation energy of $\sim 167 \text{ kJ mol}^{-1}$.^[1] While AP is commonly used, one of its major drawbacks is its toxicity. The byproducts produced by AP upon combustion include hydrochloric acid and chlorine gas, both of which are toxic and environmentally hazardous. ^[1] As such, an environmentally benign replacement for AP which will yield similar or superior performance, is very desirable.

The potential performance advantages of energetic compounds with cage-like structures are illustrated by 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzian (CL-20), heptanitrocubane (HNC), and octanitrocubane (ONC), which are arguably among the most energetic compounds known. The performances of CL-20^[2] and ONC are predicted to be approximately 14% and 15-30% better, respectively, than HMX^[3,4], the most powerful standard explosive used by the military. The increase in performance seen in these species comes from several properties directly attributed to the cage conformation, including increased density and potential energy. Because of their compact structures, the density of these materials is larger than conventional energetic materials, with ONC having the largest density of any known CHNO-containing compound of $\sim 2.1 \text{ g cm}^{-3}$ ^[4,5], whereas HMX and TNT have densities of ~ 1.9 and 1.6 g cm^{-3} respectively^[4]. The majority of the improved performance can be attributed to the fact that these structures harness a tremendous amount of potential

energy due to the inherent internal strain in such molecules. This is reflected in the heats of formation for these species, which are: ONC (1.09 kJ g^{-1}) ^[5] > CL-20 ($\sim 0.97 \text{ kJ g}^{-1}$) ^[6] > HMX (0.25 kJ g^{-1}) ^[7]. A recent study^[8] has shown that all of the additional energy exhibited by these cage species comes directly from the strain due to the cage structure. In the case of ONC, the cubane framework is responsible for the majority of the energy, whereas in CL-20 it is the resulting or enhanced strain among the NO_2 ligands.^[8] While there has been a significant amount of work on the use of cage structures for fuels^[2-6,8,9], none have been investigated as potential oxidizers. This study aims to investigate the feasibility of a novel N-O cage oxidizer, specifically N_2O_3 , for use as the replacement of AP.

The planar isomer of N_2O_3 has been well studied for the role it plays in the atmospheric NO_x cycle as a reservoir for NO and NO_2 ^[10], which are pollutants in the troposphere and can contribute to ozone depletion in the stratosphere. N_2O_3 has also been investigated as a reactive nitrogen oxide species (RNOS) relevant to numerous human diseases^[11]. N_2O_3 is known to exist as three different isomers. The global minimum is planar, with a weak N-N bond (ON-- NO_2), and has been experimentally observed ^[12,13] and can isomerize to the slightly less stable C_{2v} -symmetric planar isomer $O=N-O-N=O$.^[13] A third isomer, cis-trans N_2O_3 has also been recently verified in an argon matrix ^[14]. These studies have also been thoroughly supported by numerous theoretical works ^[15]. Nitrogen oxide rings and cages have been theoretically studied ^[16-18], including the cage isomer of N_2O_3 , and shown to be promising high energy density materials (HEDMs) due to their high exothermicity upon degradation. However, not all of these clusters are sufficiently stable to be practical HEDMs. Nonetheless it has been shown that there are numerous stable N-O clusters, with activation energies greater than 125 kJ mol^{-1} ^[17]. Furthermore, it has also been shown that the addition of external covalent oxygens to nitrogen clusters have a

stabilizing effect, increasing the activation barriers to unimolecular dissociation.[18]

This paper uses *ab initio* methods to investigate the feasibility of an energetic oxidizer in the form of the cage isomer NO_3N , shown in Figure 1 and hereafter denoted as $\text{c-N}_2\text{O}_3$, which is the simplest of the family of $\text{N}_{2x}\text{O}_{3x}$ cage molecules. The feasibility of $\text{c-N}_2\text{O}_3$ as a potential energetic oxidizer is assessed in this study by computed heats of formation and combustion relative to other common oxidizers, and its stability with respect to unimolecular and bimolecular decomposition.

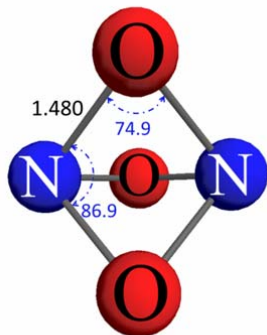


Figure 1. CCSD(T)/aug-cc-pVQZ geometry of $\text{c-N}_2\text{O}_3$. Bond lengths in Å and angles in degrees.

2 Results and Discussion

The D_{3h} -symmetric 2cage structure of N_2O_3 ($\text{c-N}_2\text{O}_3$), as seen in Figure 1, is a local minimum on the N_2O_3 potential energy surface. The N-O bond lengths of $\text{c-N}_2\text{O}_3$ are 1.480 Å, which unsurprisingly are rather long compared to what is experimentally seen in other N-O containing species, with the average experimental N-O single bond length being 1.365 ± 0.1 Å according to the NIST database[19]. The long N-O bond lengths are consistent with the tremendous amount of strain in $\text{c-N}_2\text{O}_3$, which is further exhibited in both the N-O-N and O-N-O bond angles of $\text{c-N}_2\text{O}_3$. The N-O-N and O-N-O angles in $\text{c-N}_2\text{O}_3$ are 74.9° and 86.9° respectively, compared to the previously calculated N-O-N angle of 112.6° in N_2O_5 and the experimental average of 116.3° for O-N-O. These extremely strained bond angles contribute to the large enthalpy of formation of $\text{c-N}_2\text{O}_3$ of 8.0 kJ g^{-1} , calculated using G3(MP2), which is nearly 8 times larger than that of ONC. The large enthalpy of formation of $\text{c-N}_2\text{O}_3$, coupled with its high estimated density of 1.93 g cm^{-3} obtained using the density models of Rice and Byrd,[20] makes this an attractive potential ingredient for advanced oxidizers. The electronic stability of $\text{c-N}_2\text{O}_3$ is indicated by its HOMO-LUMO gap of $1483.2 \text{ kJ mol}^{-1}$ and a vertical excitation to the triplet state of $551.0 \text{ kJ mol}^{-1}$ calculated at the MP2/aug-cc-pVDZ level of theory.

The predicted performance of $\text{c-N}_2\text{O}_3$ as an oxidizer is illustrated in Table 1, which compares the ideal enthalpies of combustion of several fuel/oxidizer combinations. For example, the combustion enthalpy

of pure bulk aluminum with ammonium perchlorate (AP) is $-1659 \text{ kJ mol}^{-1}$ or -30.7 kJ per gram of aluminum. Replacement of AP with $\text{c-N}_2\text{O}_3$ as the oxidizer increases the combustion exothermicity by nearly 570 kJ mol^{-1} to $-2228 \text{ kJ mol}^{-1}$, or -41.3 kJ per gram of fuel. Besides yielding a significant performance increase, use of $\text{c-N}_2\text{O}_3$ as the oxidizer precludes the generation of environmentally hazardous HCl as a combustion byproduct.

Table 1. Calculated enthalpies of combustion(kJ mol^{-1})

Fuel	Oxidizer	Combustion Reaction ^a	ΔH_{comb} ^b
$\text{Al}_{(\text{s})}$	$\text{NH}_4\text{ClO}_{4(\text{s})}$	$2\text{Al}_{(\text{s})} + \text{NH}_4\text{ClO}_{4(\text{s})} \rightarrow \text{Al}_2\text{O}_{3(\text{l})} + \frac{1}{2}\text{N}_{2(\text{g})} + \frac{1}{2}\text{H}_{2(\text{g})} + \text{HCl}_{(\text{g})} + \text{H}_2\text{O}_{(\text{g})}$	-1658.9 (-30.7)
$\text{Al}_{(\text{s})}$	$\text{c-N}_2\text{O}_{3(\text{g})}$	$2\text{Al}_{(\text{s})} + \text{c-N}_2\text{O}_{3(\text{g})} \rightarrow \text{Al}_2\text{O}_{3(\text{l})} + \text{N}_{2(\text{g})}$	-2228.3 (-41.3)
$\text{n-C}_6\text{H}_{14(\text{l})}$	$\text{O}_{2(\text{l})}$	$\text{C}_6\text{H}_{14(\text{l})} + \frac{13}{2}\text{O}_{2(\text{l})} \rightarrow 6\text{CO}_{(\text{g})} + 7\text{H}_2\text{O}_{(\text{g})}$	-2157.3 (-25.1)
$\text{n-C}_6\text{H}_{14(\text{l})}$	$\text{c-N}_2\text{O}_{3(\text{g})}$	$\text{C}_6\text{H}_{14(\text{l})} + \frac{13}{3}\text{c-N}_2\text{O}_{3(\text{g})} \rightarrow 6\text{CO}_{(\text{g})} + 7\text{H}_2\text{O}_{(\text{g})} + \frac{13}{3}\text{N}_{2(\text{g})}$	-4790.6 (-55.7)
$\text{MMH}_{(\text{l})}$	$\text{N}_2\text{O}_{4(\text{l})}$	$\text{CN}_2\text{H}_{6(\text{l})} + \text{N}_2\text{O}_{4(\text{l})} \rightarrow \text{CO}_{(\text{g})} + 3\text{H}_2\text{O}_{(\text{g})} + 2\text{N}_{2(\text{g})}$	-870.6 (-18.9)
$\text{MMH}_{(\text{l})}$	$\text{N}_2\text{O}_{4(\text{g})}$	$\text{CN}_2\text{H}_{6(\text{l})} + \text{N}_2\text{O}_{4(\text{g})} \rightarrow \text{CO}_{(\text{g})} + 3\text{H}_2\text{O}_{(\text{g})} + 2\text{N}_{2(\text{g})}$	-899.2 (-19.5)
$\text{MMH}_{(\text{l})}$	$\text{c-N}_2\text{O}_{3(\text{g})}$	$\text{CN}_2\text{H}_{6(\text{l})} + \frac{4}{3}\text{c-N}_2\text{O}_{3(\text{g})} \rightarrow \text{CO}_{(\text{g})} + 3\text{H}_2\text{O}_{(\text{g})} + \frac{13}{3}\text{N}_{2(\text{g})}$	-1700.4 (-37.0)

^aExperimental enthalpies of formation (kJ mol^{-1}) taken from the NIST Chemistry WebBook. ^bEnthalpies of combustion at $T=298\text{K}$. Values in parentheses are enthalpies per gram of fuel (kJ g^{-1}).

Table 1 also shows the combustion enthalpies of n-hexane ($\text{n-C}_6\text{H}_{14}$), used here as a simple model for a hydrocarbon-based fuel such as RP-1. Using liquid oxygen (LOX) as the oxidizer yields a combustion enthalpy of $-2157 \text{ kJ mol}^{-1}$ (-25.1 kJ per gram of n-hexane). The combustion enthalpies are more than doubled ($-4791 \text{ kJ mol}^{-1}$; -55.7 kJ per gram of n-hexane) when $\text{c-N}_2\text{O}_3$ is used in place of LOX. As a final example, the combustion enthalpy of monomethylhydrazine (MMH) with liquid nitrogen tetroxide is -871 kJ mol^{-1} (18.9 kJ per gram of MMH) or -899 (19.5 kJ per gram of MMH) kJ mol^{-1} when N_2O_4 is in the gas phase. With $\text{c-N}_2\text{O}_3$ as the oxidizer in place of N_2O_4 , the combustion enthalpy of MMH is nearly doubled, to $-1700 \text{ kJ mol}^{-1}$ (-37.0 kJ per gram MMH). In summary, the data in Table 1 clearly illustrate the theoretical performance improvements in combustion enthalpies when using $\text{c-N}_2\text{O}_3$ in place of conventional oxidizers.

Naturally with such geometric strain and high heat of formation, it is important to understand the barriers to thermal decomposition of $\text{c-N}_2\text{O}_3$. The potential energy surface (PES) for unimolecular decomposition has been investigated at the CCSD(T)/CBS level of theory. As seen in Figure 2, decomposition is initiated with the simultaneous breaking of two N-O bonds in $\text{c-N}_2\text{O}_3$, with a relatively small barrier of 23.6 kJ mol^{-1} via the transition state labeled TS1. This saddle point leads to formation of intermediate INT1, also referred to as cis-trans N_2O_3 in the literature[13]. At this point, the PES splits into two distinct pathways. The kinetically favored path passes

Running title

through TS2, with a barrier of 15.6 kJ mol^{-1} with respect to INT1. Along this path, an NO moiety undergoes internal rotation to form the symmetric C_{2v} isomer, sym- N_2O_3 . Through TS3, with a barrier of 57.1 kJ mol^{-1} with respect to INT1, an NO moiety dissociates from the central oxygen in INT1 and reattaches to the nitrogen atom to form the thermodynamically favored asymmetric planar N_2O_3 isomer.

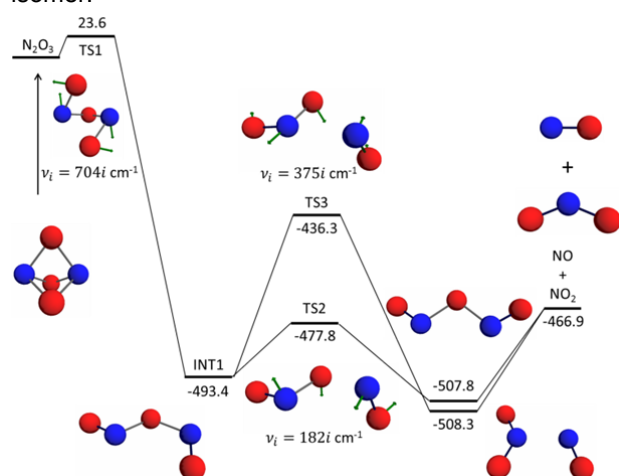


Figure 2. Potential energy surface of the unimolecular decomposition of c- N_2O_3 . Structures and relative energies calculated at the CCSD(T)/aug-cc-pVQZ and CCSD(T)/CBS levels, respectively. Energies are in kJ mol^{-1} .

Both of these planar N_2O_3 species are expected to further decompose into NO and NO_2 due to the tremendous amount of energy released from the initial bond breaking of c- N_2O_3 .

As is evident from the calculated PES, c- N_2O_3 has the potential to be a very energetic oxidizer, as indicated by the large amount of energy released upon decomposition. However, the kinetic stability of c- N_2O_3 is marginal, as the barrier for unimolecular decomposition is only 23.6 kJ mol^{-1} , which is far lower than some of the more common explosives such as RDX[21] and CL-20[22] with unimolecular decomposition barriers of 151.0 – 162.8 and $191.6 \text{ kJ mol}^{-1}$ respectively. As the stability is of concern with such a low barrier to the unimolecular decomposition, it is also important to investigate the possibility of bimolecular decomposition. This was investigated by calculating the (c- N_2O_3)₂ bimolecular interaction potential, which is shown in Figure 3. Although not apparent on the energy scale in Figure 3, the c- N_2O_3 dimer is weakly bound by 14.2 kJ mol^{-1} relative to the separated monomers. Also shown in Figure 3 is a transition state for the intermolecular decomposition, which has a barrier of $100.8 \text{ kJ mol}^{-1}$ (at the MP2/aug-cc-pVDZ level) with respect to the c- N_2O_3 dimer. This transition state is similar to the unimolecular decomposition in opening the cage structure. However, in the bimolecular decomposition, a single N-O bond scission per c- N_2O_3 occurs, in contrast to two N-O bond scissions in the unimolecular decomposition shown in Figure 2. However, the

bimolecular barrier is over 4 times as large as the unimolecular decomposition barrier. This result is similar to the behavior of the isoelectronic “CLL-1” species[23] in which bimolecular decomposition has an energetic barrier 3.45 times greater than that of the unimolecular decomposition. Therefore, it is anticipated that decomposition of c- N_2O_3 will be dominated by unimolecular processes.

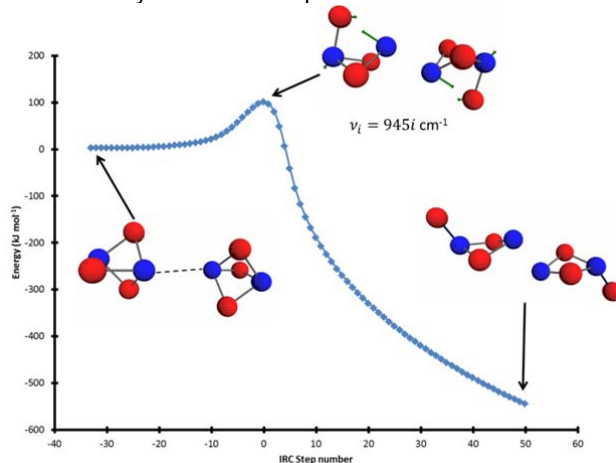


Figure 3. Intrinsic Reaction Coordinate (IRC) for the c- N_2O_3 dimer transition state

3 Theoretical Methods

All geometries and frequencies of c- N_2O_3 and its unimolecular decomposition intermediates and products are calculated at the CCSD and CCSD(T)/aug-cc-pV(D,T,Q)Z levels of theory. All structural and vibrational data reported herein are at the CCSD(T)/aug-cc-pVQZ level of theory and all energetic data at the CCSD(T)/CBS level. The cartesian coordinates and harmonic vibrational frequencies at the CCSD(T)/aug-cc-pVQZ for all relevant species of the unimolecular decomposition can be found in the supplementary information, along with all CCSD and CCSD(T)/aug-cc-pV(D,T,Q) energies and CBS data. First order saddle points have been verified as such via the presence of a single negative eigenvalue (corresponding to an imaginary harmonic vibrational frequency) of the diagonalized mass-weighted hessian matrix. Intrinsic reaction coordinate (IRC) calculations[24] are performed to trace the minimum energy path from each saddle point to reactants and products. The open shell species have been calculated using restricted open-shell Hartree-Fock (ROHF) reference wave functions and the completely renormalized coupled cluster method, CR-CC(2,3),D.[25] The energies of all species were extrapolated to the complete basis set limit (CBS) using the linear Schwenke extrapolation [26], as shown in eq. 1, where in this study $E^C(X_2)$ refers to energies using the aug-cc-pVTZ basis and $E^C(X_1)$ to the aug-cc-pVQZ energies, C is for the separated SCF, CCSD and (T) energy components and F is an optimized parameter for each, all of which are available in the supplemental section.

$$E_{\infty}^C = [E^C(X_2) - E^C(X_1)]F_{X_2}^C + E^C(X_1) \quad (1)$$

The geometries and transition states used for investigating the c-N₂O₃ dimer interaction as a model for the condensed phase were calculated at the MP2/aug-cc-pVDZ level. The reactants and products linked to the transition states found here were confirmed by IRC calculations. All of the calculations used in this study were performed using the GAMESS quantum chemistry code^[27].

4 Conclusion

In this paper c-N₂O₃ was investigated as a potential energetic oxidizer. c-N₂O₃ was found to be a local minima on the N₂O₃ potential energy surface, with a large heat of formation of 604.25 kJ mol⁻¹ (7.95 kJ g⁻¹) due to a tremendous amount of strain in the N-O-N and O-N-O angles. The gas phase unimolecular decomposition of c-N₂O₃ has a small barrier of 23.6 kJ mol⁻¹ to form NO + NO₂. Further investigation into the decomposition pathway of c-N₂O₃ was done by looking at the bimolecular decomposition as a simple probe of stability in the condensed phase. The bimolecular decomposition reaction pathway has an activation barrier of over 100 kJ mol⁻¹ and takes place via rupture of a single N-O bond in each c-N₂O₃ monomer, as opposed to two N-O bond scissions in unimolecular decomposition. Therefore, c-N₂O₃ is unlikely to be a practical energetic oxidizer due to its low unimolecular decomposition barrier.

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