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Theoretical Study on $H_3N_3O_3$ for Solid Rocket Propellant

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Due to high enthalpies of formation with good oxygen balance, there is a continuing demand for new nitrogen-rich energetic materials.[1] It is worthy to point out that decomposition of those compounds affords large volumes of environmentally friendly and green dinitrogen molecule. Prior to undertaking a possibly costly and time-consuming synthesis, a theoretical approach can be taken to evaluate proposed compounds. The development of accurate models and simulations of high-energetic, dense materials has been continuously pursued with the advent of computational capabilities.[2]

Ball calculated the enthalpies of formation and proton affinities of derivatives of hydrazine and showed that those are useful for solid rocket motor.[3] Interestingly, dinitrogen tetraoxide, which was known as a self-igniting mixture, is currently used in liquid-fueled rockets and in the Space Shuttle's orbital maneuvering subsystem.[4] So combination of characteristics of N_2H_4 with N_2O_4 within a molecule will be a promising strategy for the design of energetic materials.

In the present study, we evaluate and predict the suitability of 1,3,5,2,4,6-trioxatriazine molecule as potential oxidizer model for solid rocket propulsion. The structure, stability, and detonation properties of the compound will be presented. We will demonstrate that there are still rooms for the development of new high energy materials based on relatively small molecules.

All calculations for structures and energies were carried out using the Gaussian G03W (revision B.03) program package.[5] The enthalpies and free energies were calculated using the complete basis set (CBS) method of Petersson and coworkers and a MP4(SDQ)/6-31+(d,p) calculation is used to approximate higher order contributions. In this study we applied the modified CBS-4M method (M referring to the use of Minimal Population localization) which is a reparametrized version of the original CBS-4 method and also includes some additional empirical corrections.[6]

The molecular structure of $H_3N_3O_3$ was fully optimized without symmetry constraints at HF/6-31G* level of theory to give a *C*s symmetric structure in chaired form (Fig. 1). The O-N distances are 1.445-1.473 Å. The averaged dihedral angle made by two oxygen atoms around one nitrogen atom is 104.5°, which is smaller than that by two nitrogen atoms around one oxygen atom by 0.5°. The molecule, 1,3,5-trinitrohexahydro-1,3,5-triazine (RDX), consists of alternative CH_2 and N-NO_2 groups in a puckered ring.[7]

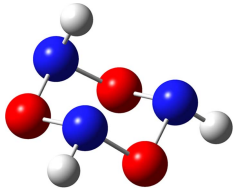

Figure 1. Optimized Molecular Structure for $H_3N_3O_3$.

The enthalpies of formation of the gas-phase species were computed according to the atomization energy method.[8] Using the values the gas phase enthalpy of formation of 1,3,5,2,4,6-trioxatriazine could be calculated to $\Delta H_f°$ (g,$H_3N_3O_3$) = +100.6 kcal/mol. The melting point of $H_3N_3O_3$ was taken to be equal to that of $(CH_2O)_3$ (120 °C).[9] The enthalpy of sublimation for $H_3N_3O_3$ was estimated as 17.7 kcal/mol according to Trouton's rule.[10] With the estimated sublimation enthalpy, the enthalpy of formation for solid 1,3,5,2,4,6-trioxatriazine can be calculated to $\Delta H_f°$ (s,$H_3N_3O_3$) = +82.9 kcal/mol. Using the correlation $H_m = U_m + nRT$,[11] the $\Delta U_f°(s)$ value can be obtained as +3809 kJ/kg. The density of $H_3N_3O_3$ was calculated to ρ ($H_3N_3O_3$) = 1.60 g/cm^3 from the molecular volume.[12]

The detonation parameters of $H_3N_3O_3$ were calculated for different densities using the EXPLO5 (version 5.04) computer program (Table 1).[13] Table 1 shows the detonation parameters of the $H_3N_3O_3$ molecule used in an aluminized formulation in comparison to those of the highly energetic RDX. Because $H_3N_3O_3$ compound is an oxidizer with a positive oxygen balance, the value should be close to zero by using Al as an explosive. The increased Al content of a parent molecule raises all of the predicted detonation temperatures, pressure, and velocities and accordingly produces much higher amounts of heat of detonation. Usually a good oxygen balance results in more negative heat of detonation and therefore leads to a better performance of the explosive. It is unexpected that relatively small molecule without polynitro groups like $H_3N_3O_3$ compound can perform as RDX.

In this study we assumed firing the rocket motor against ambient atmosphere as it is commonly the case for tactical missiles. The theoretical characteristics of the rocket motor

Table 1. Detonation Parameters for $H_3N_3O_3$ Depending on Its Density

	100% $H_3N_3O_3$	80% $H_3N_3O_3$, 20% Al (w/w)	100% RDX
ρ (g/cm^3)	1.60	1.82	1.80
Ω (%)	+25.8	+2.8	-21.6
Q_v (kJ/kg)	-7642	-12347	-6111
T_{ex} (K)	5250	7360	4390
$P_{C\text{-}J}$ (kbar)	336	363	337
D (m/s)	9004	9224	8868
V_0 (L/kg)	903	598	739

ρ = density, Ω = oxygen balance, Q_v = heat of detonation, T_{ex} = detonation temperature, $P_{C\text{-}J}$ = detonation pressure at the Chapman-Jouguet point, D = detonation velocity, V_0 = volume of detonation gases, RDX = 1,3,5-trinitrohexahydro-1,3,5-triazine.

propellant may be derived from the analysis of the expansion of the combustion products through the nozzle. The specific impulse I_{sp}^* is an important parameter for the characterization of rocket propellants and can be interpreted as the effective exhaust velocity of the combustion gases when exiting the expansion nozzle.

Table 2 summarized the calculated rocket propellant performance parameters for an assumed chamber pressure of 70 bar for the neat propellants covalent $H_3N_3O_3$ used as monopropellants and for aluminized formulations in which the Al content has been varied in order to achieve optimal performance. It shows that a formulation with 20% Al gives better combustion properties than neat $H_3N_3O_3$ molecule. It also implies the specific impulse of 80% $H_3N_3O_3$ with 20% Al formulation is much higher than that of the conventional 70%/30% of AP/Al theoretically.

The results clearly indicate that a formulation of 20% Al gives optimal performance and is comparable to a mixture of 70% AP and 30% Al. To be solid rocket motors, they should be chlorine or perchlorate-free, close to 2.0 g/cm^3 in density, low vapor pressure, and less sensitive than PETN (pentaerythritol tetranitrate). Our results suggest that $H_3N_3O_3$ molecule might be the promising candidate for solid rocket motors. However, nitro-substituted trioxatriazine, 2,4,6-trinitro-1,3,5, 2,4,6-trioxatriazine, can easily be oxidized to give $6NO_2$ molecules, therefore it is not useful as energetic materials.

From this theoretical study on $H_3N_3O_3$, the suggested molecule shows superior detonation parameters compared to the highly energetic RDX, especially when used in a aluminized formulation and the specific impulse of the chlorine and perchlorate-free formulation with Al indicates a much higher calculated performance than that of the conventional AP/Al formulation. It also shows very good predicted properties as a monopropellant for solid rocket motors. All the results obtained here should encourage synthetic works to prepare on a laboratory scale.

Table 2. Combustion Properties (Solid Rocket Motor) of Neat $H_3N_3O_3$ and a Formulation with 20% Al (Frozen Expansion)[a]

	$H_3N_3O_3$	80% $H_3N_3O_3$, 20% Al	70% AP, 30% Al
condition	isobaric	isobaric	isobaric
p (bar)	70	70	70
ρ (g/cm^3)	1.60	1.82	2.18
Ω (%)	25.8	2.84	-2.8
Q_p (kJ/kg)	-5697	-7492	-6787
T_{comb} (K)	3721	4454	4290
I_{sp}^* (s)	283	292	243

[a]Q_P = heat of isobaric combustion, T_{comb} = combustion temperature, I_{sp}^* = specific impulse, AP = ammonium perchlorate.

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References

1. (a) Srinivas, D.; Ghule, V. D.; Muralidharan, K.; Jenkins, H. D. B. *Chem. Asian J.* **2013**, *8*, 1023. (b) Gao, H.; Shreeve, J. M. *Chem. Rev.* **2011**, *111*, 7377.
2. Rice, B. M.; Byrd, E. F. C.; Mattson, W. D. Computational Aspects of Nitrogen-Rich HEDMs. In *High Energy Density Materials*; Klapötke, T. M., Ed.; Structure and Bonding *125*; Springer: Berlin, 2007; pp 153-104.
3. Ball, D. W. *J. Mol. Struct.-Theochem* **2006**, *773*, 1 and references therein.
4. Greenwood, N. N.; Earnshow, A. *Chemistry of the Elements*; Pergamon Press: Oxford, 1984.
5. Frish, J.; *et al. Gaussian 03, Revision A.1*; Gaussian, Inc.: Pittsburgh PA, 2003.
6. Montgomery, J.; Frisch, M. J.; Ochterski, J. W.; Petersson, G. A. *J. Chem. Phys.* **2000**, *112*, 6532 and references therein.
7. Millar, D. I. A.; Oswald, I. D. H.; Barry, C.; Francis, D. J.; Marshall, W. G.; Pulham, C. R.; Cumming, A. S. *Chem. Commun.* **2010**, *46*, 5662 and references therein.
8. (a) Byrd, E. F. C.; Rice, B. M. *J. Phys. Chem A* **2006**, *110*, 1005. (b) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *J. Chem. Phys.* **1997**, *106*, 1063. (c) Linstrom, P. J.; Mallard, W. G. *NIST Chemistry Webbook*, NIST Standard Reference Database Number 69, Gaithersburg, MD; June, 2005 (http://webbook.nist.gov).
9. http://www.sigmaaldrich.com/catalog.
10. Westwell, M. S.; Searle, M. S.; Wales, D. J.; Williams, D. H. *J. Am. Chem. Soc.* **1995**, *117*, 5013.
11. Köhler, J.; Meyer, R. *Explosivstoffe*, 9th ed.; Wiley-VCH: Weinheim, 1998.
12. Klapötke, T. M.; Ang, H. G. *Propellants, Explos., Pyrotech.* **2001**, *26*, 221.
13. Sućeska, M. *EXPLO5 Program*: Zagreb, Croatia, 2010.
14. Klapötke, T. M. *Chemistry of High-Energy Materials*, 2nd ed.; de Gruyter: Berlin, New York, 2012.