INITIAL REACTIONS OF GAS-PHASE THERMOLYSIS OF BICYCLOOCTOGEN FROM HIGHLY ACCURATE QUANTUM CHEMICAL CALCULATIONS

I. N. Melnikov[1], N. V. Muravyev[1], A. N. Pivkina[1], and V. G. Kiselev[1,2,3]

[1]N. N. Semenov Federal Research Center for Chemical Physics of the Russian Academy of Sciences, 4 Kosygin Str., Moscow 119991, Russian Federation
[2]Institute of Chemical Kinetics and Combustion, Siberian Branch of the Russian Academy of Sciences, Novosibirsk, Russian Federation
[3]Novosibirsk State University, Novosibirsk, Russian Federation

Abstract: Cis-1,3,4,6-tetranitrooctahydroimidazo [4,5-d] imidazole (BCHMX) is a promising novel energetic component of solid propellants and plastic bonded explosives. Even though the thermolysis of BCHMX in the solid state and solution has been actively studied using both experimental and theoretical tools, its decomposition mechanism remains unclear. The present authors studied the primary gas-phase reactions of BCHMX thermolysis using the highly accurate and reliable DLPNO-CCSD(T) quantum chemical methodology. A full set of 9 gas-phase conformers of BCHMX has been considered and those never discussed before have been identified. For all conformers, the radical decomposition (viz., $N–NO_2$ bond scission) and a number of molecular channels, such as HONO elimination and several other isomerization reactions, have been considered. Among the studied channels, the dominant role belongs to the radical decomposition with a $N–NO_2$ bond energy of $\sim$ 41 kcal/mol. The activation barriers of other molecular channels turned out to be higher than 50 kcal/mol.

Keywords: bicyclo-HMX; quantum chemistry; thermal decomposition; kinetics gas-phase reactions; primary decomposition channels

DOI: 10.30826/CE19120416

Acknowledgments

The work was supported by the Russian Science Foundation (project No. 19-73-20217).

References

1. Klasovitý, D., S. Zeman, A. Růžička, M. Jungová, and M. Roháč. 2009. cis-1,3,4,6-Tetranitrooctahydroimidazo-[4,5-d]imidazole (BCHMX), its properties and initiation reactivity. *J. Hazard. Mat.* 164:954–961. doi: 10.1016/j.jhazmat.2008.08.106.
2. Koppes, W. M., M. Chaykovsky, H. G. Adolph, R. Gilardi, and C. George. 1987. Synthesis and structure of some peri-substituted 2,4,6,8-tetraazabicyclo[3.3.0]octanes. *J. Org. Chem.* 52(6):1113–1119. doi: 10.1021/jo00382a025.
3. Eck, G., and M. Piteau. 1997. Process for the synthesis of 2,4,6,8-tetranitro-2,4,6,8-tetraazabicyclo (3.3.0) octane. U.S. Patent 5569032.
4. Gilardi, R., J. L. Flippen-Anderson, and R. Evans. 2002. Cis-2,4,6,8-Tetranitro-1H,5H-2,4,6,8-tetraazabicyclo[3.3.0]octane, the energetic compound 'bicyclo-HMX.' *Acta Cryst. E* 58:972–974. doi: 10.1107/S1600536802013582.
5. Molt, R. W., T. Watson, Jr., A. P. Bazanté, and R. J. Bartlett. 2013. The great diversity of HMX conformers: Probing the potential energy surface using CCSD(T). *J. Phys. Chem. A* 117:3467–3474. doi: 10.1021/jp311073m.
6. Turker, L., and T. Atalar. 2006. Ab initio and DFT study on 1,4-dinitroglycoluril configurational isomers: cis-DINGU and trans-DINGU. *J. Hazard. Mat.* 137(1):47–56. doi: 10.1016/j.jhazmat.2006.01.060.
7. Turker, L. 2018. A DFT study on TNGU isomers and aluminizedcis-TNGU composites. *Defence Technology* 14(2):109–118. doi: 10.1016/j.dt.2017.08.001.
8. Qiu, L., X. H. Ju, and H. M. Xiao. 2005. Density functional theory study of solvent effects on the structure and vibrational frequencies of Tetranitrotetraazabicyclooctane "bicyclo-HMX." *J. Chin. Chem. Soc. Taip.* 52:405–413. doi: 10.1002/jccs.200500061.
9. Qiu, L., H. Xiao, X. Gong, X. Ju, and W. Zhu. 2007. Crystal density predictions for nitramines based on quantum chemistry. *J. Hazard. Mat.* 141(1):280-8. doi: 10.1016/j.jhazmat.2006.06.135.
10. Zeman, S., A. K. Hussein, A. Elbeih, and M. Jungova. 2018. cis-1,3,4,6-Tetranitrooctahydroimidazo-[4,5-d]imidazole (BCHMX) as a part of explosive mix-

tures. *Defence Technology* 14(5):380–384. doi: 10.1016/j.dt.2018.04.002.

11. Goncharov, T. K., V. V. Dubikhin, G. M. Nazin, V. G. Prokudin, and Z. G. Aliev. 2011. Thermal decomposition of cis-2,4,6,8-tetranitro-1H,5H-2,4,6,8-tetraazabicyclo[3.3.0]octane. *Russ. Chem. Bull.* 60(6):1138–1143. doi: 10.1007/s11172-011-0178-8.
12. Yan, Q.-L., S. Zeman, X.-H. Zhang, J. Málek, and W.-X. Xie. 2015. The mechanisms for desensitization effect of synthetic polymers on BCHMX: Physical models and decomposition pathways. *J. Hazard. Mater.* 294(1):145–157. doi: 10.1016/j.jhazmat.2015.03.063.
13. Zeman, S., A. K. Hussein, A. Elbeih, and M. Jungova. 2018. cis-1,3,4,6-Tetranitrooctahydroimidazo-[4,5-d]imidazole (BCHMX) as a part of explosive mixtures. *Defence Technology* 14:380–384. doi: 10.1016/j.dt.2018.04.002.
14. Zeman, S., A. K. Hussein, M. Jungova, and A. Elbeih. 2019. Effect of energy content of the nitraminic plastic bonded explosives on their performance and sensitivity characteristics. *Defence Technology* 15:488–494. doi: 10.1016/j.dt.2018.12.003.
15. Hussein, A. K., A. Elbeih, and S. Zeman. 2017. Thermal decomposition kinetics and explosive properties of a mixture based on cis-1,3,4,6-tetranitrooctahydroimidazo-[4,5-d]imidazole and 3-nitro-1,2, 4-triazol-5-one (BCHMX/NTO). *Therm. Acta* 655:292–301. doi: 10.1016/j.tca.2017.07.016.
16. Hussein, A. K., S. Zeman, A. Elbeih, and M. Jungova. 2018. The effect of different additives on safety manipulation of cis-1,3,4,6-tetranitrooctahydroimidazo-[4,5-d]imidazole (BCHMX). *4th Conference (International) on Engineering, Applied Sciences and Technology "Exploring Innovative Solutions for Smart Society." MATEC Web Conf.* 192.
17. Hussein, A. K., A. Elbeih, and S. Zeman. 2018.Thermoanalytical study of a melt cast composition based on cis-1,3,4,6-tetranitrooctahydroimidazo-[4,5 d]imidazole (BCHMX)/trinitrotoluene (TNT) compared with traditional compositions. *Thermochim. Acta* 666:91–102. doi: 10.1016/j.tca.2018.06.006.
18. Elbeiha, A., A. K. Hussein, T. Elshenawy, *et al.* 2019. Enhancing the explosive characteristics of a Semtex explosive by involving admixtures of BCHMX and HMX. *Defence Technology*. doi: 10.1016/j.dt.2019.05.012.
19. Stepanov, R. S., L. A. Kruglyakova, and A. M. Astakhov. 2006. Kinetics of thermal decomposition of some N-nitroamines possessing two fused five-membered rings. *Russ. J. Gen. Chem.* 76(12):1974–1975. doi: 0.1134/S1070363206120309.
20. Ye, C., Q. An, W. A. Goddard, *et al.* 2015. Initial decomposition reactions of Bicyclo-HMX [BCHMX or cis-1,3,4,6-Tetranitrooctahydroimidazo-[4,5-d]imidazole] from quantum molecular dynamics simulations. *J. Phys. Chem. C* 119:2290–2295. doi: 10.1021/jp510328d.
21. Yan, Q.-L., S. Zeman, R. Svoboda, and A. Elbeih. 2012. Thermodynamic properties, decomposition kinetics and reaction models of BCHMX and its Formex bonded explosive. *Therm. Acta* 547(10):150–160. doi: 10.1016/j.tca.2012.08.018.
22. Elbeih, A., M. Abd-Elghany, and T. M. Klapötke. 2017. Kinetic parameters of PBX based on Cis-1,3,4,6-tetranitroocta-hydroimidazo-[4,5-d] imidazole obtained by isoconversional methods using different thermal analysis techniques. *Propell. Explos. Pyrot.* 42(5):468–476. doi: 42.10.1002/prep.201700032.
23. Zhao, Y., and D. G. Truhlar. 2008. The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, non-covalent interactions, excited states, and transition elements: Two new functionals and systematic testing of four M06-class functionals and 12 other functionals. *Theor. Chem. Acc.* 120(1):215–241. doi: 10.1007/s00214-007-0310-x.
24. Frisch, M. J., G. W. Trucks, H. B. Schlegel, *et al.* 2013. Gaussian 09, revision D.01. Wallingford, CT: Gaussian, Inc.
25. Neese, F. 2018. Software update: The ORCA program system, version 4.0: Software update. *WIREs Comput. Mol. Sci.* 8:e1327. doi: 10.1002/wcms.1327.
26. Kiselev, V. G., and C. F. Goldsmith. 2019. Accurate prediction of bond dissociation energies and barrier heights for high-energy caged nitro and nitroamino compounds using a coupled cluster theory. *J. Phys. Chem. A* 123(23):4883–4890. doi: 10.1021/acs.jpca.9b01506.
27. Supady, A., V. Blum, and C. Baldauf. 2015. First-principles molecular structure search with a genetic algorithm. *J. Chem. Inf. Model.* 55(11):2338–2348. doi: 10.1021/ acs.jcim.5b00243.

Received November 20, 2019

Contributors

Melnikov Igor N. (b. 1995) — junior research scientist, N. N. Semenov Federal Research Center for Chemical Physics of the Russian Academy of Sciences, 4 Kosygin Str., Moscow 119991, Russian Federation; igor.n.melnikov@ya.ru

Muravyev Nikita V. (b. 1985) — Candidate of Science in technology, senior research scientist, N. N. Semenov Federal Research Center for Chemical Physics of the Russian Academy of Sciences, 4 Kosygin Str., Moscow 119991, Russian Federation; muravyev.nikita@ya.ru

Pivkina Alla N. (b. 1958) — Doctor of Science in technology, head of laboratory, N. N. Semenov Federal Research Center for Chemical Physics of the Russian Academy of Sciences, 4 Kosygin Str., Moscow 119991, Russian Federation; alla_pivkina@mail.ru

Kiselev Vitaly G. (b. 1984) — Candidate of Science in physics and mathematics, assistant professor, deputy head of department, Novosibirsk State University, Novosibirsk, Russian Federation; senior research scientist, Institute of Chemical Kinetics and Combustion, Siberian Branch of the Russian Academy of Sciences, Novosibirsk, Russian Federation; senior research scientist, N. N. Semenov Federal Research Center for Chemical Physics of the Russian Academy of Sciences, 4 Kosygin Str., Moscow 119991, Russian Federation; kiselev@phys.nsu.ru