ENERGETIC POTENTIAL OF TRIS(PYRROLO)-, TRIS(DIAZOLO)BENZENES, AND 1,3,5-AZINES AS MODEL COMPONENTS OF SOLID PROPELLANTS

V. V. Parakhin[1], V. M. Volokhov[2], D. B. Lempert[2], E. S. Amosova[2], and V. V. Voevodin[3]

[1]N. D. Zelinsky Institute of Organic Chemistry of the Russian Academy of Sciences, 47 Leninsky Prosp., Moscow 119991, Russian Federation

[2]Federal Research Center for Problems of Chemical Physics and Medicinal Chemistry of the Russian Academy of Sciences, 1 Prosp. Academician Semenov, Chernogolovka, Moscow Region 142432, Russian Federation

[3]Research Computing Center of the M. V. Lomonosov Moscow State University, 1-4 Leninskie Gory, Moscow 119234, Russian Federation

Abstract: Enthalpies of formation of a number of hypothetical tris(pyrrolo)- and tris(diazolo)benzenes and 1,3,5-azines in the condensed phase have been estimated on the basis of calculated values of enthalpies of formation of these compounds in the gas phase. Their efficiency as components (main energetic component or binder plasticizer) of model solid composite propellants or as energetic component for increasing ballistic efficiency of nonmetallized solid propellants for gas-generator engines has been analyzed. It has been established that polynitro-derivatives of the proposed pyrrole-, pyrazole-, and imidazole-containing tetracycles can be used as plasticizers of the active binder in the compositions of model solid composite propellants including those based on aluminum hydride, metallic aluminum, and those without metal providing higher ballistic efficiency on all three stages of rocket systems in comparison with similar propellants using the most promising modern plasticizers, for example, dinitrofurazan, nitroglycerin, or tetranitromethane. It is shown by calculations that the studied tetracycles which do not contain nitro groups can serve as high-enthalpy components in propellants for gas-generator engines providing high ballistic efficiency relative to the binary formulation of a dispersant with rubber.

Keywords: high-energy materials; solid propellants; gas-generator motor; tetracycles; tris(pyrrolo)benzenes; tris(pyrrolo)1,3,5-azines; tris(diazolo)benzenes; tris(diazolo)1,3,5-azines; enthalpy of formation; effective impulse

DOI: 10.30826/CE24170311 **EDN:** GGBJPJ

Figure Captions

Figure 1 Structures of the objects of the study — energetic tris(pyrrolo)-, tris(diazolo)benzenes, and 1,3,5-azines

Figure 2 The $I_{ef}(2)$ (*a*) and $I_{ef}(3)$ (*b*) values of formulations containing 27 %(vol.) PMVT (polymethylvinyl tatrazole) binder/plasticizer = 1 : 4 (IIa, IIb, IVa, IVb, VIa–VIc, DNF (dinitrofurazane), NG (nitroglycerin), or TNM (tetranitromethane)), 25 %(wt.) aluminum hydride and ammonium dinitramide (ADN) (rest)

Figure 3 The $I_{ef}(1)$ (*a*), $I_{ef}(2)$ (*b*), and $I_{ef}(3)$ (*c*) values of formulations containing 50 %(wt.) HMX, 19 %(vol.) PMVT binder/plasticizer = 1 : 4 (IIa, IIb, IVa, IVb, VIa–VIc, DNF, NG, or TNM), 15 %(wt.) Al, and ammonium perchlorate (AP) (rest)

Figure 4 The $I_{ef}(1)$ (*a*), $I_{ef}(2)$ (*b*), and $I_{ef}(3)$ (*c*) values of formulations containing 50 %(wt.) HMX, 19 %(vol.) PMVT binder/plasticizer = 1 : 4 (IIa, IIb, IVa, IVb, VIa–VIc, DNF, NG, or TNM), and AP (rest)

Figure 5 Dependence of $Q_v(1500)$ values of propellant compositions containing rubber SKI-3, $Az(O)NH_2$, and high-enthalpy component (HEC) Ia (*1*), Ib (*2*), IIIa (*3*), IIIb (*4*), Va (*5*), and Vb (*6*) at $T_{ad} = 1500 \pm 5$ K as well as dicyanobenzene (*7*), phenazine N-oxide (*8*), naphtacene (*9*), and anthracene (*10*) on the nature of the HEC and its mass content

Table Captions

Table 1 Calculated parameters of basic properties of investigated tetracycles of subgroups I–VI

Table 2 Ballistic characteristics of propellants containing ADN, aluminum hydride, and 27 %(vol.) PMVT-based binder with plasticizer IIa, IIb, Ia, Ib, VIa–VIc, DNF, NG, or TNM

Table 3 Ballistic characteristics of propellants containing HMX, AP, Al, and 19 %(vol.) PMVT-based binder with plasticizer IIa, IIb, Ia, Ib, VIa–VIc, DNF, NG, or TNM

Table 4 Ballistic characteristics of propellants containing HMX, AP, and 19 %(vol.) PMVT-based binder with plasticizer IIa, IIb, Ia, Ib, VIa–VIc, DNF, NG, or TNM

Table 5 Densities $Q_u(1500)$ and $Q_v(1500)$ of propellants containing SKI-3, Az(O)NH_2, and energetic compounds Ia, Ib, IIIa, IIIb, Va, and Vb at $T_{\text{ad}} = 1500 \pm 5$ K

Acknowledgments

The work was performed under the topics of state assignments, state registration Nos. 124020100045-5 and 124013100856-9. Calculations by resource-intensive methods were carried out under the grant of the Russian Science Foundation (project No. 23-71-00005).

References

1. Zlotin, S. G., I. L. Dalinger, N. N. Makhova, and V. A. Tartakovsky. 2020. Nitro compounds as the core structures of promising energetic materials and versatile reagents for organic synthesis. *Russ. Chem. Rev.* 89(1):1–54. doi: 10.1070/RCR4908.
2. Tang, J., H. Yang, Y. Cui, and G. Cheng. 2021. Nitrogen-rich tricyclic-based energetic materials. *Materials Chemisty Frontiers* 5(19):7108–7118. doi: 10.1039/D1QM00916H.
3. Bennion, J. C., and A. J. Matzger. 2021. Development and evolution of energetic cocrystals. *Accounts Chem. Res.* 54(7):1699–1710. doi: 10.1021/acs.accounts.0c00830.
4. Zlotin, S. G., A. M. Churakov, M. P. Egorov, L. L. Fershtat, M. S. Klenov, I. V. Kuchurov, N. N. Makhova, G. A. Smirnov, Y. V. Tomilov, and V. A. Tartakovsky. 2021. Advanced energetic materials: Novel strategies and versatile applications. *Mendeleev Commun.* 31(6):731–749. doi: 10.1016/j.mencom.2021.11.001.
5. Zhou, J., J. Zhang, B. Wang, L. Qiu, R. Xu, and A. B. Sheremetev. 2021. Recent synthetic efforts towards high energy density materials: How to design high-performance energetic structures? *FirePhysChem.* 2(2):83–139. doi: 10.1016/j.fpc.2021.09.005.
6. Luo, Y., W. Zheng, X. Wang, and F. Shen. 2022. Nitrification progress of nitrogen-rich heterocyclic energetic compounds: A review. *Molecules* 27(5):1465. doi: 10.3390/molecules27051465.
7. Yount, J., and D. G. Piercey. 2022. Electrochemical synthesis of high-nitrogen materials and energetic materials. *Chem. Rev.* 122(9):8809–8840. doi: 10.1021/acs.chemrev.1c00935.
8. Singh, R. P., H. Gao, D. T. Meshri, and J. M. Shreeve. 2007. Nitrogen-rich heterocycles. *High energy density materials. Structure and bonding*. Ed. T. M. Klapötke. Berlin, Heidelberg: Springer. 125:35–84. doi: 10.1007/430_2006_055.
9. Xie, C., L. Pei, J. Cai, P. Yin, and S. Pang. 2022. Imidazole-based energetic materials: A promising family of N-heterocyclic framework. *Chem. — Asian J.* 17(21):e202200829. doi: 10.1002/asia.202200829.
10. She, W., Z. Xu, L. Zhai, J. Zhang, J. Huang, W. Pang, and B. Wang. 2022. Synthetic methods towards energetic heterocyclic N-oxides via several cyclization reactions. *Crystals* 12(10):1354. doi: 10.3390/cryst12101354.
11. Fershtat, L. L. 2023. Recent advances in thesynthesis and performance of 1,2,4,5-tetrazine-based energetic materials. *FirePhysChem.* 3(1):78–87. doi: 10.1016/j.fpc.2022.09.005.
12. Gao, H., Q. Zhang, and J. M. Shreeve. 2020. Fused heterocycle-based energetic materials. *J. Mater. Chem. A* 8(8):4193–4216. doi: 10.1039/C9TA12704F.
13. Samsonov, V. A., L. B. Volodarskii, V. L. Korolev, and G. K. Khisamutdinov. 1993. Synthesis of benzotristriazole. 4-nitrobenzo[1,2-d:3,4-d′]bistriazole and 4,4′-dicarboxy-5,5′-1H-1,2,3-triazole. *Chem. Heterocyc. Compd.* 29(10):1169–1171. doi: 10.1007/BF00538063.
14. Khisamutdinov, G. K., V. L. Korolev, T. N. Parkhomenko, V. M. Sharonova, E. S. Artem'eva, I. Sh. Abdrakhmanov, S. P. Smirnov, and B. I. Ugrak. 1993. Synthesis and properties of 1,2,4-triazolo[4,3-d]-1,2,4-triazolo-[3,4-f]furazano[3,4-b]pyrazines. *Russ. Chem. Bull.* 42(10):1700–1702. doi: 10.1007/BF00697044.
15. Starchenkov, I. B., V. G. Andrianov, and A. F. Mishnev. 1999. The chemistry of furazano-[3,4-b]pyrazine. 7. Properties of 5,6-diamino-and 5,6-dihydrazino-furazano[3,4-b]pyrazine. *Chem. Heterocyc. Compd.* 35(4):499–508. doi: 10.1007/BF02319341.
16. Thottempudi, V., F. Forohor, D. A. Parrish, and J. M. Shreeve. 2012. Tris(triazolo)benzene and its derivatives: High-density energetic materials. *Angew. Chem. Int. Edit.* 51(39):1–6. doi: 10.1002/anie.201205134.
17. Sheremetev, A. B., V. L. Korolev, A. A. Potemkin, N. S. Aleksandrova, N. V. Palysaeva, T. H. Hoang, V. P. Sinditskii, and K. Yu. Suponitsky. 2016. Oxygen-rich 1,2,4-Triazolo[3,4-d]-1,2,4-triazolo[3,4-f]furazano[3,4-b]pyrazines as energetic materials. *Asian J. Org. Chem.* 5(11):1388–1397. doi: 10.1002/ajoc.201600386.
18. Lempert, D. B., and A. B. Sheremetev. 2018. Polynitromethyl derivatives of furazano[3,4-e]di([1,2,4]triazolo)-[4,3-a:3,4-c]pyrazine as components of solid composite propellants. *Russ. Chem. Bull.* 67(11):2065–2072. doi: 10.1007/s11172-018-2330-1.
19. Qu, Y., Q. Zeng, J. Wang, G. Fan, J. Huang, and G. Yang. 2018. Synthesis and properties for benzotriazole nitrogen oxides (BTZO) and tris[1,2,4]triazolo[1,3,5]triazine derivatives. *Int. J. Materials Science Applications* 7(2):49–57. doi: 10.11648/j.ijmsa.20180702.13.

20. Yang, X., X. Lin, L. Yang, and T. Zhang. 2018. A novel method to synthesize stable nitrogen-rich polynitrobenzenes with π-stacking for high-energy-density energetic materials. *Chem. Commun.* 54(73):10296–10299. doi: 10.1039/c8cc05413d.

21. Dorofeenko, E. M., A. B. Sheremetev, and D. B. Lempert. 2019. Effects of aluminum additions on the specific impulse of propellants based on high-enthalpy oxidizers containing NO_2 and NF_2 groups. *Russ. J. Phys. Chem. B* 13(5):755–762. doi: 10.1134/S1990793119040183.

22. Curtiss, L. A., P. C. Redfern, and K. Raghavachari. 2007. Gaussian-4 theory using reduced order perturbation theory. *J. Chem. Phys.* 127(12):124105. doi: 10.1063/1.2770701.

23. Frisch, M. J., G. W. Trucks, H. B. Schlegel, *et al.* 2010. Gaussian 09, Revision B.01. Wallingford, CT: Gaussian, Inc.

24. Volokhov, V., E. Amosova, V. Parakhin, D. Lempert, and I. Akostelov. 2023. Quantum-chemical study of some tris(pyrrolo)benzenes and tris(pyrrolo)-1,3,5-triazines. *Supercomputing.* Eds. V. Voevodin, S. Sobolev, M. Yakobovskiy, and R. Shagaliev. Lecture notes in computer science ser. 14388:177–189. Cham: Springer. doi: 10.1007/978-3-031-49432-1_14.

25. Westwell, M. S., M. S. Searle, D. J. Wales, and D. Williams. 1995. Empirical correlations between thermodynamic properties and intermolecular forces. *J. Am. Chem. Soc.* 117(18):5013–5015. doi: 10.1021/ja00123a001.

26. Kotomin, A. A., and A. S. Kozlov. 2005. *Plotnost' organicheskikh soedineniy. Metod rascheta plotnosti po vkladam fragmentov molekul* [Density of organic compounds. Method for calculating density from contributions of molecular fragments]. St. Petersburg: SPbGTI (TU). 38 p.

27. Volokhov, V. M., V. V. Parakhin, E. S. Amosova, A. V. Volokhov, D. B. Lempert, and T. S. Zyubina. 2024. Quantum-chemical calculations of the enthalpy of formation for 5/6/5 tricyclic tetrazine derivatives annelated with nitrotriazoles. *Russ. J. Phys. Chem. B* 18(1):28–36. doi: 10.1134/S1990793124010196.

28. Lempert, D. B., G. N. Nechiporenko, and G. B. Manelis. 2006. Energetic characteristics of solid composite propellants and ways of energy increasing. *Cent. Eur. J. Energ. Mat.* 3(4):73–87.

29. Trusov, B. G. 2002. Programmnaya sistema TERRA dlya modelirovaniya fazovykh i khimicheskikh ravnovesiy [Program system TERRA for simulation phase and thermal chemical equilibrium]. *14th Symposium (International) on Chemical Thermodynamics Proceedings.* St. Petersburg: Research Institute of Chemistry, St. Petersburg State University. 483–484.

30. Zyuzin, I. N., I. Yu. Gudkova, and D. B. Lempert. 2020. Energetic capabilities of N-dinitro- and N-trinitromethyl derivatives of nitroazoles as composite solid propellant components. *Russ. J. Phys. Chem. B* 14(5):804–813. doi: 10.1134/S1990793120050140.

31. Zyuzin, I. N., I. Y. Gudkova, and D. B. Lempert. 2021. Energy abilities of certain derivatives of 1,2,4,5-tetrazine N-oxides as components of solid composite rocket propellants. *Russ. J. Phys. Chem. B* 15(4):611–621. doi: 10.1134/S1990793121040138.

32. Gudkova, I. Yu., I. N. Zyuzin, and D. B. Lempert. 2022. Energy capabilties of 5,5′-azotetrazol-1,1′-diol and its onium salts as components of solid composite propellants. *Russ. J. Phys. Chem. B* 16(1):58–65. doi: 10.1134/S1990793122010067.

33. Zyuzin, I. N., I. Yu. Gudkova, and D. B. Lempert. 2022. Energy capabilities of some oxidizers with two N-trinitromethylazole fragments in one molecule as components of composite energy systems. *Russ. J. Phys. Chem. B* 16(5):902–911. doi: 10.1134/S1990793122050141.

34. Pavlovets, G. Ya., and V. I. Tsutsuran. 2009. *Fiziko-khimicheskie svoystva porokhov i raketnykh topliv* [Physical and chemical properties of gunpowders and rocket propellants]. Moscow: Publishing House of the Russian Ministry of Defense. 248 p.

35. Lempert, D. B., L. S. Yanovsky, V. V. Raznoschikov, I. S. Averkov, and A. M. Stolnikov. 2022. O vozmozhnosti povysheniya energeticheskikh kharakteristik nemetallizirovannykh tverdykh gazogeneratornykh topliv [On the possibility of increasing the energy characteristics of nonmetallized solid gas-generator fuels]. *Boepripasy i spetskhimiya* [Munitions and Special Chemistry] 3:36–44.

36. Zyuzin, I. N., E. M. Dorofeenko, S. I. Soglasnova, and D. B. Lempert. 2023. Energeticheskie aspekty ispol'zovaniya dobavok k binarnym tverdym toplivam dlya gazogeneratornykh dvigateley [Energy aspects of the use of additives to binary solid fuels for gas-generator engines]. *Boepripasy i spetskhimiya* [Munitions and Special Chemistry] 2:70–78.

37. Kizin, A. N., P. A. Dvorkin, G. L. Ryzhova, and Yu. A. Lebedev. 1986. Parameters for calculation of standard enthalpies of formation of organic compounds in the liquid state. *B. Acad. Sci. USSR Ch.* 35(2):343–346.

38. Yanovsky, L. S., D. B. Lempert, V. V. Raznoschikov, I. S. Averkov, and A. M. Stolnikov. 2023. Otsenka effektivnosti primeneniya napolniteley v tverdykh nemetallizirovannykh gazogeneratornykh toplivakh [Evaluation of fillers in solid nonmetallized gas-generator fuels]. *Boepripasy i spetskhimiya* [Munitions and Special Chemistry] 3:98–107.

Received May 17, 2024

Contributors

Parakhin Vladimir V. (b. 1986) — Candidate of Science in chemistry, senior research scientist, N. D. Zelinsky Institute of Organic Chemistry of the Russian Academy of Sciences, 47 Leninsky Prosp., Moscow 119991, Russian Federation; parakhin@ioc.ac.ru

Volokhov Vadim M. (b. 1950) — Doctor of Science in physics and mathematics, professor, chief research scientist, Federal Research Center for Problems of Chemical Physics and Medicinal Chemistry of the Russian Academy of Sciences, 1 Prosp. Academician Semenov, Chernogolovka, Moscow Region 142432, Russian Federation; vvm@icp.ac.ru

Lempert David B. (b. 1946) — Candidate of Science in chemistry, chief research scientist, Federal Research Center for Problems of Chemical Physics and Medicinal Chemistry of the Russian Academy of Sciences, 1 Prosp. Academician Semenov, Chernogolovka, Moscow Region 142432, Russian Federation; lempert@icp.ac.ru

Amosova Elena S. (b. 1981) — research scientist, Federal Research Center for Problems of Chemical Physics and Medicinal Chemistry of the Russian Academy of Sciences, 1 Prosp. Academician Semenov, Chernogolovka, Moscow Region 142432, Russian Federation; aes@icp.ac.ru

Voevodin Vladimir V. (b. 1962) — Doctor of Science in physics and mathematics, Corresponding Member of the Russian Academy of Sciences, professor, director, Research Computing Center of the M. V. Lomonosov Moscow State University, 1-4 Leninskie Gory, Moscow 119234, Russian Federation; voevodin@parallel.ru