1,1′-AZO-BIS[3-(NITRO-NNO-AZOXY)-1H-1,2,4-TRIAZOLE]: DECOMPOSITION KINETICS AND COMBUSTION BEHAVIORS

L. Ya. Melnikova[1], V. P. Sinditskii[1], N. E. Leonov[2], and M. S. Klenov[2]

[1]D. Mendeleev University of Chemical Technology of Russia, 9 Miusskaya Sq., Moscow 125047, Russian Federation

[2]N. D. Zelinsky Institute of Organic Chemistry of the Russian Academy of Sciences, 47 Leninsky Prosp., Moscow 119334, Russian Federation

Abstract: The thermal decomposition of 1,1′-azo-bis[3-(nitro-NNO-azoxy)-1H-1,2,4-triazole] (ANAzTr) has been studied under nonisothermal and isothermal conditions. The obtained activation energy of ANAzTr decomposition in the liquid phase is 37.6 kcal/mol which is close to the calculated dissociation energy of the N–NO_2 bond (33–34 kcal/mol). Based on the analysis of decomposition products, the possible mechanism of ANAzTr decomposition was proposed. The ANAzTr compound proved to be a fast burning substance, superior to tetrazene in all parameters (stability, density, detonation velocity and pressure, and combustion temperature). Combustion of ANAzTr, despite the very short residence time of the substance in the condensed phase, is determined by the reaction of its decomposition at surface temperatures. The dependence of the surface temperature on the pressure was estimated.

Keywords: 1,1′-azo-bis[3-(nitro-NNO-azoxy)-1H-1,2,4-triazole]; nitro-NNO-azoxy group; thermal stability; decomposition kinetics; combustion

DOI: 10.30826/CE25180313 **EDN:** QEBZSE

Figure Captions

Figure 1 Structural formula of 1,1′-azo-bis[3-(nitro-NNO-azoxy)-1H-1,2,4-triazole]

Figure 2 Structural formula of 1,1′-azo-bis[3-nitro-1H-1,2,4-triazole]

Figure 3 Gas release curves for ANAzTr isothermal decomposition

Figure 4 Mass loss curves for ANAzTr isothermal decomposition

Figure 5 Comparison of the kinetic parameters of ANAzTr decomposition under nonisothermal conditions (DSC, *1*) with the decomposition data under isothermal conditions of iso-TGA (k_{isoTGA}, *2*) and manometry (*3*)

Figure 6 Dependence of the burning rate on pressure for ANAzTr (*1*) in comparison with the burning rates of CL-20 (*2*), FTDO (*3*), and tetrazene (*4*)

Figure 7 Surface temperature of ANAzTr (*1*) compared with experimental data for NTO (*2*) and NTO_2Tz (*3*)

Table Captions

Table 1 Some physicochemical properties of compound ANAzTr [6] compared with azo-bis[3-nitro-1H-1,2,4-triazole] [8, 9]

Table 2 Comparison of ANAzTr and tetrazene properties

References

1. Leonov, N. E., M. S. Klenov, O. V. Anikin, A. M. Churakov, Yu. A. Strelenko, K. A. Monogarov, and V. A. Tartakovsky. 2019. First synthesis of aliphatic nitro-NNO-azoxy compounds. *Eur. J. Org. Chem.* 2019(1):91–94. doi: 10.1007/s11172-024-4269-8.
2. Anikin, O. V., N. E. Leonov, M. S. Klenov, A. M. Churakov, A. A. Voronin, A. A. Guskov, N. V. Muravyev, Yu. A. Strelenko, I. V. Fedyanin, and V. A. Tartakovsky. 2019. An energetic (nitro-NNO-azoxy)triazolo-1,2,4-triazine. *Eur. J. Org. Chem.* 2019(26):4189–4195. doi: 10.1002/ejoc.201900314.
3. Leonov, N. E., M. S. Klenov, O. V. Anikin, A. M. Churakov, Y. A. Strelenko, A. A. Voronin, D. B. Lempert, N. V. Muravyev, I. V. Fedyanin, S. E. Semenov, and V. A. Tartakovsky. 2020. Synthesis of new energetic materials based on furazan rings and nitro-NNO-azoxy groups. *ChemistrySelect* 5(39):12243–12249. doi: 10.1002/slct.202003182.
4. Wang, Y., S. Li, Y. Li, R. Zhang, D. Wang, and S. Pang. 2014. A comparative study of the structure, energetic performance and stability of nitro-NNO-azoxy substituted explosives. *J. Mater. Chem. A* 2(48):20806–20813. doi: 10.1039/C4TA04716H.
5. Leonov, N. E., M. S. Klenov, A. M. Churakov, T. S. Konkova, E. A. Miroshnichenko, Yu. N. Matyushin, N. V. Muravyev, and V. A. Tartakovsky. 2022. Experimental enthalpies of formation and other physicochemical characteristics of compounds containing C–NO_2 and C–N(O)=N–NO_2 groups: A comparison. *Russ. Chem. B.* 71(8):1634–1640. doi: 10.1007/s11172-022-3572-5.

6. Klenov, M. S., N. E. Leonov, A. M. Churakov, and V. A. Tartakovsky. 21.10.2022. 1,1′-(E)-Diazen-1,2-diilbis[3-(nitro-NNO-azoksi)-1H-1,2,4-triazol] i sposob ego polucheniya [1,1′-(E)-Diazen-1,2-diylbis[3-(nitro-NNO-azoxy)-1H-1,2,4-triazole] and method for its production]. Patent RF No. 2782118.
7. Klenov, M. S., A. M. Churakov, A. A. Voronin, D. B. Vinogradov, and V. A. Tartakovsky. 2024. Development of new nitrogen–oxygen systems in the Laboratory of Chemistry of Nitro Compounds at the Zelinsky Institute of Organic Chemistry of the Russian Academy of Sciences. *Russ. Chem. B.* 73(5):1473–1494. doi: 10.1007/s11172-024-4269-8.
8. Yin, P., D. A. Parrish, and J. M. Shreeve. 2014. N-diazo-bridged nitroazoles: Catenated nitrogen-atom chains compatible with nitro functionalities. *Chem. — Eur. J.* 20(22):6707–6712. doi: 10.1002/chem.201402762.
9. Klenov, M. S., D. B. Lempert, A. A. Konnov, D. A. Gulyaev, I. A. Vatsadze, Yu. N. Matyushin, E. A. Miroshnichenko, A. B. Vorobyev, Ya. O. Inozemtsev, T. S. Konkova, A. V. Inozemtsev, A. N. Pivkina, A. O. Dmitrienko, and V. A. Tartakovsky. 2022. 1,2-Bis (nitroazol-1-yl)diazenes: Improved methods of synthesis, determination of the enthalpies of formation, and calculations of main energy characteristics of solid composite propellants based on these compounds. *Russ. Chem. B.* 71(6):1123–1134. doi: 10.1007/s11172-022-3512-4.
10. Kissinger, H. E. 1957. Reaction kinetics in differential thermal analysis. *Anal. Chem.* 29(11):1702–1706. doi: 10.1021/ac60131a045.
11. Robertson, A. J. B. 1949. The thermal decomposition of explosives. Part II. Cyclotrimethylenetrinitramine and cyclotetramethylenetetranitramine. *T. Faraday Soc.* 45:85–93. doi: 10.1039/TF9494500085.
12. Churakov, A. M., S. L. Ioffe, and V. A. Tartakovskii. 1996. Synthesis of l-aryl-2-nitrodiazene 1-N-oxides. *Mendeleev Commun.* 1(6):20–22. doi: 10.1070/MC1996v006n01ABEH000560.
13. Churakov, A. M. 2005. Tsiklicheskie sopryazhennye poliazotnye sistemy novogo tipa [Cyclic conjugated polynitrogen systems of a new type]. Moscow: N. D. Zelinsky Institute of Organic Chemistry of the Russian Academy of Sciences. D.Sc. Diss. 224 p.
14. Sinditskii, V. P., V. Yu. Egorshev, M. V. Berezin, V. V. Serushkin, Yu. M. Milekhin, S. A. Gusev, and A. A. Matveev. 2003. Zakonomernosti i mekhanizm goreniya vysokoenergeticheskogo karkasnogo nitramina geksanitrogeksaazaizovyurtsitana [Combustion behaviors of high-energy framework nitramine hexanitrohexaazaisowurtzitane]. *Khim. Fiz.* 22(7):69–74.
15. Sinditskii, V. P., A. V. Burzhava, V. Yu. Egorshev, A. B. Sheremetev, and V. P. Zelenov. 2013. Combustion of furazanotetrazine dioxide. *Combust. Explo. Shock Waves* 49(1):117–120. doi: 10.1134/S0010508213010139.
16. Fogelzang, A. E., V. Yu. Egorshev, A. Yu. Pimenov, A. R. Saklantii, V. P. Sinditskii, and B. S. Svetlov. 1985. Issledovanie statsionarnogo goreniya initsiiruyushchikh vzryvchatykh veshchestv pri vysokikh davleniyakh [Study of stationary combustion of primary explosives at high pressures]. *Dokl. Akad. Nauk SSSR* 282(6):1449–1452.
17. Kolesov, V. I., K. O. Kapranov, A. V. Tkacheva, and I. A. Kulagin. 2021. Explosive characteristics of tetrazene and MTX-1. *Combust. Explo. Shock Waves* 57(3):350–355. doi: 10.1134/S0010508221030102.
18. Stull, D. R., E. F. Westrum, and G. C. Sinke. 1969. *The chemical thermodynamics of organic compounds*. New York, NY: J. Wiley. 865 p.
19. Ilyushin, M. A., I. V. Shugaley, I. V. Tselinsky, and A. V. Garabadgiu. 2012. Nekotorye ekologicheskie problemy ispol'zovaniya energonasyshchennykh soedineniy dlya sredstv initsiirovaniya i puti ikh resheniya [Some environmental problems of using energetic compounds for initiation means and ways of their solution]. *Ekologicheskaya khimiya* [Ecological Chemistry] 21(3):154–163.
20. Bagal, L. I. 1975. *Khimiya i tekhnologiya initsiiruyushchikh vzryvchatykh veshchestv* [Chemistry and technology of primary explosives]. Moscow: Mashinostroenie. 456 p.
21. Meyer, R., J. Köhler, and A. Homburg. 2007. *Explosives*. 6th ed. Weinheim: Wiley-VCH Verlag GmbH. 442 p.
22. Sumin, A. I., B. N. Kondrikov, V. N. Gamezo, and V. M. Raikova. 1998. Shock and detonation general kinetics and thermodynamics in reactive systems computer package. *11th Detonation Symposium (International) Proceedings*. Snowmass, CO. 30–35.
23. Belov, G. B. 1998. Thermodynamic analysis of combustion products at high temperature and pressure. *Propell. Explos. Pyrot.* 23:86–89. doi: 10.1002/(SICI)1521-4087(199804)23:2<86::AID-PREP86>3.0.CO;2-2.
24. Sinditskii, V. P., V. Y. Egorshev, and M. V. Berezin. 2003. Gorenie energoemkikh tsiklicheskikh nitraminov [Combustion of energetic cyclic nitramines] *Khim. Fiz.* 22(4):56–63.
25. Sinditskii, V. P., V. Y. Egorshev, V. V. Serushkin, A. I. Levshenkov, M. V. Berezin, and S. A. Filatov. 2010. Combustion of energetic materials governed by reactions in the condensed phase. *Int. J. Energetic Materials Chemical Propulsion* 9(2):147–192. doi: 10.1615/IntJEnergeticMaterialsChemProp.v9.i2.30.
26. Sinditskii, V. P., S. P. Smirnov, and V. Y. Egorshev. 2007. Thermal decomposition of NTO: An explanation of the high activation energy. *Propell. Explos. Pyrot.* 32(4):277–287. doi: 10.1002/prep.200700029.
27. Rudakov, G. F., I. B. Kozlov, N. V. Boev, S. S. Zinchenko, L. Y. Melnikova, V. Y. Egorshev, and V. P. Sinditskii. 2021. Synthesis and physicochemical properties of energetic 1,2,4,5-tetrazinyl derivatives of 5-nitro-2,4-dihydro-1,2,4-triazol-3-one. *ChemistrySelect* 6(30):7654–7662. doi: 10.1002/slct.202102160.

Received January 6, 2025
After revision January 14, 2025
Accepted January 27, 2025

Contributors

Melnikova Ludmila Ya. (b. 2000) — postgraduate student, Department of Chemistry and Technology of Organic Nitrogen Compounds, D. Mendeleev University of Chemical Technology of Russia, 9 Miusskaya Sq., Moscow 125047, Russian Federation; melnikova.l.i@muctr.ru

Sinditskii Valeriy P. (b. 1954) — Doctor of Science in chemistry, professor, dean, Chemical Engineering Department, D. Mendeleev University of Chemical Technology of Russia, 9 Miusskaya Sq., Moscow 125047, Russian Federation; vps@muctr.ru

Leonov Nikita E. (b. 1996) — research engineer, N. D. Zelinsky Institute of Organic Chemistry of the Russian Academy of Sciences, 47 Leninsky Prosp., Moscow 119334, Russian Federation; leonovne@ioc.ac.ru

Klenov Mikhail S. (b. 1987) — Candidate of Science in chemistry, head of laboratory of Chemistry of Nitro Compounds, N. D. Zelinsky Institute of Organic Chemistry of the Russian Academy of Sciences, 47 Leninsky Prosp., Moscow 119334, Russian Federation; klenov@ioc.ac.ru