

MECHANISM OF DECOMPOSITION OF SUBSTITUTED (DINITROPYRAZOLYL)AZOXYFURAZANS

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Abstract: The thermal decomposition of substituted (dinitropyrazolyl) azoxyfurazans was studied under non-isothermal and isothermal conditions. It turned out that the thermal decomposition of some azoxy compounds in open systems can occur without significant heat release. Possible pathways of decomposition of the studied compounds are considered. In all cases they begin with the cleavage of the bond between the azoxy group and the furazan ring. The insignificant heat effect of the initial stage of decomposition of azoxy compounds makes it difficult to determine the actual kinetic parameters by differential scanning calorimetry (DSC).

Keywords: thermal decomposition; decomposition kinetics; azoxy compounds; (dinitropyrazolyl)azoxyfurazanes

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Figure Captions

Figure 1 Structural formulae of the investigated substances

Figure 2 Gas release curves for isothermal decomposition of compounds **1–3**: 1—**1**, 220 °C; 2—**2**, 220 °C; and 3—**3**, 200 °C

Figure 3 Comparison of kinetic parameters of decomposition of compound **1** under nonisothermal conditions (DSC) in closed crucibles (empty signs) and crucibles with a hole (filled signs) with decomposition data under isothermal conditions of iso-TGA ($k_{\text{iso-TGA}}$) and manometry (k_{MM})

Figure 4 Comparison of kinetic parameters of decomposition of compound **2** under nonisothermal conditions (DSC) in closed crucibles ($k_{\text{N}_2\text{O}}$) and in crucibles with a hole (triangles, peaks 1 and 2) with decomposition data under isothermal conditions (k_1 and k_2)

Figure 5 Comparison of kinetic parameters of decomposition of compound **3** under nonisothermal conditions (DSC) in closed crucibles ($k_{\text{N}_2\text{O}}$) and in crucibles with a hole (triangles, peaks 1 and 2) with data of decomposition under isothermal conditions by iso-TGA ($k_{\text{iso-TGA}}$) and manometry (k_1 and k_2)

References

1. Sheremetev, A. B., V.O. Kulagina, N.S. Aleksandrova, D.E. Dmitriev, Y.A. Strelenko, V.P. Lebedev, and Y.N. Matyushin. 1998. Dinitro trifurazans with oxy, azo, and azoxy bridges. *Propell. Explos. Pyrot.* 23(3):142–149.
2. Zhang, J., and J.M. Shreeve. 2015. Nitroaminofurazans with azo and azoxy linkages: A comparative study of structural, electronic, physicochemical, and energetic properties. *J. Phys. Chem. C* 119(23):12887–12895.
3. Konnov, A. A., I. M. Dubrovin, M. S. Klenov, et al. 2021. Synthesis of energetic compounds bearing a (3,4-dinitro-1H-pyrazol-1-yl)-NNO-azoxy group. *Russ. Chem. B.* 70:2189–2194.
4. Sinditskii, V.P., A.V. Burzhava, and A.B. Sheremetev. 2021. Macrocyclic tetra (azo-) and tetra (azoxyfurazan)s: Comparative study of decomposition and combustion with linear analogs. *Energetic Materials Frontiers* 2(2):87–95.
5. Klenov, M. S., D. B. Lempert, A. A. Konnov, et al. 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.
6. Konnov, A. A., M. S. Klenov, A. M. Churakov, I. L. Dallinger, Y.A. Strelenko, I. V. Fedyanin, D. B. Lempert, A. N. Pivkina, T. S. Kon'kova, Y.N. Matyushin, and V. A. Tartakovskiy. 2023. Novel energetic furazans containing isomeric N-(azoxy)-dinitropyrazole moieties: Synthesis, characterization and comparison of properties. *Energetic Materials Frontiers* 4(1):1–9.
7. Spence, G. G., E. C. Taylor, and O. Buchardt. 1970. Photochemical reactions of azoxy compounds, nitrones, and aromatic amine N-oxides. *Chem. Rev.* 70(2):231–265.
8. Wang, L., Ch. Yi, H. Zou, et al. 2011. Theoretical study on the thermal decomposition mechanism of 3,3'-dinitro-4,4'-azoxyfurazan. *Comput. Theor. Chem.* 963(1):135–140.
9. Sinditskii, V. P., M. C. Vu, V. P. Shelaputina, A. B. Sheremetev, and N. S. Alexandrova. 2007. Study on ther-

- mal decomposition and combustion of insensitive explosives 3,3'-diamino-4,4'-azofurazan (DAAzF) and 3,3'-diamino-4,4'-azoxyfurazan (DAAF). *7th Autumn Seminar (International) on Propellants, Explosives and Pyrotechnics Proceedings*. Beijing, China: Beijing University Press. 7:422–428.
10. Sinditskii, V.P., M.C. Vu, A.B. Sheremetev, and N.S. Alexandrova. 2008. Study on thermal decomposition and combustion of insensitive explosive 3,3'-diamino-4,4'-azofurazan (DAAzF). *Thermochim. Acta* 473(1-2):25–31.
 11. Gorn, M. V., K. A. Monogarov, I. L. Dalinger, I. N. Melnikov, V. G. Kiselev, and N. V. Muravyev. 2020. Pressure DSC for energetic materials. Part 2. Switching between evaporation and thermal decomposition of 3,5-dinitropyrazole. *Thermochim. Acta* 690:178697.
 12. Prokudin, V.G., and G. M. Nazin. 1987. Gas-phase cyclodecomposition of furazan and furazan N-oxide. *B. Acad. Sci. USSR* 36(1):199–201.
 13. Kissinger, H. E. 1957. Reaction kinetics in differential thermal analysis. *Anal. Chem.* 29(11):1702–1706.
 14. Sinditskii, V.P., A.V. Burzhava, D.V. Dashko, and N.I. Shishov. 2014. Issledovanie termicheskogo raspada i goreniya 4,4-dinitro-tris-furazana (NTF) [Study of the thermal decomposition and combustion of 4,4-dinitro-tris-furazan (NTF)]. *Goren. Vzryv (Mosk.) — Combustion and Explosion* 7:346–352.
 15. Sinditskii, V.P., S. P. Smirnov, V. Yu. Egorshev, A. N. Chernyj, T. K. Shkineva, N. V. Palysaeva, K. Yu. Suponitsky, and I. L. Dalinger. 2017. Thermal decomposition peculiarities and combustion behavior of nitropyrazoles. *Thermochim. Acta* 651:83–99.

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