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ЭКСПЕРТНОЕ ЗАКЛЮЧЕНИЕ О ВОЗМОЖНОСТИ ОПУБЛИКОВАНИЯ

Руководитель-эксперт Федерального государственного бюджетного учреждения науки Института элементоорганических соединений им. А.Н.Несмеянова Российской академии наук, рассмотрев ***статью Sinditskii V.P., Burzhava A.V., Usuntsinova A.V., Egorshev V.Yu, Palysaeva N.V., Suponitsky K.Yu, Ananiev I.V., Sheremetev A.B. «Increasing the burning rate through energetic compound tuning: Hybrids of the furazan and [1,2,4]triazolo[4,3-b][1,2,4,5]tetrazine ring systems», направляемую в журнал Combustion and Flame,*** подтверждает, что в материале ***не содержатся*** сведения, предусмотренные Постановлением Правительства РФ №1233 от 30.11.1994г. и на публикацию материала ***не следует*** получать разрешение ***Минобрнауки России и/или Президиума РАН***

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Increasing the burning rate through energetic compound tuning: Hybrids of the furazan and [1,2,4]triazolo[4,3-b][1,2,4,5]tetrazine ring systems

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ABSTRACT

Combustion behavior, flame structure, and thermal decomposition of hybrid compounds based on tetrazine, triazole and furazan rings have been described. It has been found that the introduction of [1,2,4]triazolo[4,3-b][1,2,4,5] tetrazine core into the molecules of energetic materials allows obtaining energetic hybrid compounds with combustion rates greater than those of common explosive HMX and RDX. These hybrids have good thermal stability, which depends on the substituent at the furazan ring, and not on the triazolotetrazine core. Combustion with thermocouple-aided studies has shown that all triazolotetrazine hybrids are nonvolatile and have high burning surface temperatures which cause their condensed-phase combustion mechanism. Based on the condensed-phase combustion model, the constants of the leading combustion reactions were determined. It turned out that the burning rates of nitrogen-rich compounds of this study are controlled by the decomposition kinetics at surface temperature. It is shown that the two-stage decomposition of substances leads to the appearance of two regions in the burning rate-pressure dependences that related to each other by the instability region. The incorporation of the triazolotetrazine moiety into an energetic compound is a promising way to design new propellant components with high burning rates and attractive performance.

1. Introduction

Currently, hybrid compounds based on endothermic heterocycles such as furazan, tetrazole and triazole are of wide interest and importance due to their utilization in synthetic chemistry and as key backbone of energetic materials [1–7]. As a potential alternative to conventional explosives or components of rocket propellants, nitrogen-rich compounds form a promising class of energetic materials whose energy is derived, to a large degree, from their very high enthalpy of formation. The disadvantage of mononuclear furazan derivatives that prevent their practical use is high volatility. At the same time, 1,2,4,5-tetrazines and, especially, their fused derivatives are characterized by very high melting and boiling points and low volatility [8,9]. It can be assumed that the synthesis of hybrids combining tetrazine and furazan rings can eliminate the above furazan's disadvantages and will allow obtaining new compounds with a novel set of properties.

Approaches to the production of hybrid compounds whose cores are a combination of the (un)fused tetrazine ring systems with various azoles have been described previously [1,5,10–12]. However, the properties of these hybrids have not been studied in sufficient detail. First of all, the burning rate is of interest, since nitrogen-rich compounds may be used as components that lower the flame temperature of the powders, as well as combustion modifiers of the powders and solid rocket propellants [13,14].

Recently [15], it was found that the binding of the triazolotetrazine backbone with 3,5-dinitro-1H-pyrazole unit through the NH-bridge leads to an increase in the burning rate and a decrease in the pressure index of burning law, that is very important for the components of gunpowder and solid rocket propellants. In this regard, the purpose of this work is to study the effect of the triazolotetrazine moiety on the combustion

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decomposition of substances leads to the appearance of two regions in the burning-rate dependences that related to each other by the transition or instability region.

The introduction of a triazolotetrazine moiety into a molecule of energetic compounds could open a new way to advanced propellant components with high burning rates and good practical properties as thermal stability and sensitivity.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.combustflame.2019.12.006.

References

[1] I.L. Dalinger, A.V. Kormanov, K.Y. Suponitsky, N.V. Muravyev, A.B. Sheremetev, Pyrazole-tetrazole hybrid with trinitromethyl, fluorodinitromethyl, or (difluoroamino) dinitromethyl groups: high-performance energetic materials, Chem. Asian J 13 (9) (2018) 1165–1172.

[2] Y.X. Tang, C.L. He, G.H. Imler, D.A. Parrish, J.M. Shreeve, Energetic furazan-triazole hybrid with dinitromethyl and nitramino groups: decreasing sensitivity via the formation of a planar anion, Dalton Trans 48 (2019) 7677–7684.

[3] T. Wei, W. Zhu, J. Zhang, H. Xiao, DFT study on energetic tetrazolo-[1,5-*b*]-1,2,4,5-tetrazine and 1,2,4-triazolo-[4,3-b]-1,2,4,5-tetrazine derivatives, J. Hazard. Mater. 179 (1–3) (2010) 581–590.

[4] A.B. Sheremetev, N.V. Palysaeva, K.Y. Suponitsky, M.I. Struchkova, Synthesis of [1,2,4]triazolo[4,3-b]-s-tetrazines with incorporated furazan ring, Russ. Chem. Bull. 61 (1) (2012) 121–130.

[5] A.B. Sheremetev, N.V. Palysaeva, M.I. Struchkova, K.Y. Suponitsky, M.Y. Antipin, Copper-catalyzed C–N coupling reactions of nitrogen rich compounds – reaction of iodofurazans with s-tetrazinylamines, Eur. J. Org. Chem. 2012 (11) (2012) 2266–2272.

[6] S. Deswal, V.D. Ghule, T.R. Kumar, S. Radhakrishnan, Quantum-chemical design of tetrazolo[1,5-*b*][1,2,4,5]tetrazine based nitrogen-rich energetic materials, Comput. Theor. Chem. 1054 (2015) 55–62.

[7] G. Wang, T. Lu, G. Fan, H. Yin, F.X. Chen, Synthesis and properties of insensitive [1,2,4]triazolo[4,3-*b*]-1,2,4,5-tetrazine explosives, New J. Chem. 43 (4) (2019) 1663–1666.

[8] V.P. Sinditskii, V.Y. Egorshev, G.F. Rudakov, A.V. Burzhava, S.A. Filatov, L.D. Sang, Thermal behavior and combustion mechanism of high-nitrogen energetic materials DHT and BTATz, Thermochim. Acta 535 (2012) 48–57, doi:10.15372/FGV20190309.

[9] V.P. Sinditskii, V.Y. Egorshev, G.F. Rudakov, S.A. Filatov, A.V. Burzhava, High-nitrogen energetic materials of 1,2,4,5-tetrazine family: thermal and combustion behaviors, Chemical Rocket Propulsion, Springer Aerospace Technology, Springer, Switzerland, 2017, pp. 89–127.

[10] A.B. Sheremetev, N.V. Palysaeva, M.I. Struchkova, The first synthesis of 3-nitro-4-[(*s*-tetrazin-3-yl) amino]furazans, Mendeleev Commun 20 (6) (2010) 350–352.

[11] N.V. Palysaeva, K.P. Kumpan, M.I. Struchkova, I.L. Dalinger, A.V. Kormanov, N.S. Aleksandrova, V.M. Chernyshev, D.F. Pyreu, K. Yu. Suponitsky, A.B. Sheremetev, A direct approach to a 6-hetarylamino [1,2,4]triazolo[4,3-*b*][1,2,4,5] tetrazine library, Org. Lett. 16 (2) (2013) 406–409.

[12] P.A. Efimova, A.D. Borodavina, G.F. Rudakov, V.F. Zhilin, Synthesis of energetic materials based on 1,2,4-triazolo[4,3-*b*]-1,2,4,5-tetrazine, Uspekhi Khimii i Khim. Tekhn. (Adv. Chem. Chem. Techn.) 26 (2012) 105–109 in Russian.

[13] J.H. Yi, F.Q. Zhao, B.Z. Wang, Q. Liu, C. Zhou, R.Z. Hu, Y.-H. Ren, S.-Y. Xu, K.-Z. Xu, X.N. Ren, Thermal behaviors, nonisothermal decomposition reaction kinetics, thermal safety and burning rates of BTATz-CMDB propellant, J. Hazard. Mater. 181 (1–3) (2010) 432–439.

[14] J. Lavoie, C.F. Petre, S. Durand, C. Dubois, Stability and performance of gun propellants incorporating 3, 6-dihydrazino-s-tetrazine and 5-aminotetrazolium nitrate, J. Hazard. Mater. 363 (2019) 457–463.

[15] V.P. Sinditskii, S.P. Smirnov, V. Yu Egorshev, A.N. Chernyi, T.K. Shkineva, N.V. Palysaeva, K. Yu Suponitsky, I.L. Dalinger, Thermal decomposition peculiarities and combustion behavior of nitropyrazoles, Thermochim. Acta 651 (2017) 83–99, doi:10.1016/j.tca.2017.02.019.

[16] A.B. Sheremetev, N.S. Aleksandrova, N.V. Palysaeva, M.I. Struchkova, V.A. Tartakovsky, K.Yu. Suponitsky, Ionic liquids as unique solvents in one-pot synthesis of 4-(N,2,2,2-tetranitroethylamino)-3-R-furazans, Chem. Eur. J. 19 (2013) 12446–12457.

[17] A.A. Gidaspov, V.A. Zalomlenkov, V.V. Bakharev, V.E. Parfenov, E.V. Yurtaev, M.I. Struchkova, N.V. Palysaeva, K. Yu. Suponitsky, D.B. Lempert, A.B. Sheremetev, Novel trinitroethanol derivatives: high energetic 2-(2,2,2-trinitroethoxy)-1,3,5-triazines, RSC Adv. 6 (2016) 34921–34934.

[18] T.S. Kon'kova, Yu.N. Matyushin, E.A. Miroshnichenko, A.B. Vorob'ev, N.V. Palysaeva, A.B. Sheremetev, Thermochemical properties of [1,2,4]triazolo[4,3-*b*][1,2,4,5]tetrazine derivatives, Russ. J. Phys. Chem. B 14 (1) (2020) 1–5 [Khimicheskaya Fizika, 39(1) (2020) 1–5 (Engl. Transl.)].

[19] H.E. Kissinger, Reaction kinetics in differential thermal analysis, Anal. Chem. 29 (11) (1957) 1702–1706.

[20] G.B. Belov, Thermodynamic analysis of combustion products at high temperature and pressure, Prop. Explos. Pyrotech. 23 (3) (1998) 86–89.

[21] V.P. Sinditskii, W.D. He, V.V. Serushkin, A.E. Fogelzang, A.B. Sheremetev, Study on combustion of new energetic furazans, 29 International Annual Conference of ICT, Karlsruhe, FRG, 30 June -July 3, 30 (1998) 170–1–170–11.

[22] V.P. Sinditskii, M.C. Vu, A.B. Sheremetev, N.S. Alexandrova, Study on thermal decomposition and combustion of insensitive explosive 3,3′-diamino-4,4′-azofurazan (DAAzF), Thermochim. Acta 473 (1–2) (2008) 25–31.

[23] A.E. Fogelzang, V. Yu Egorshev, V.P. Sinditsky, M.D. Dutov, Combustion of nitroderivatives of azidobenzenes and benzofuroxans, Comb. Flame 87 (2) (1991) 123–135.

[24] V.P. Sinditskii, A.E. Fogelzang, V.Yu. Egorshev, V.V. Serushkin, V.I. Kolesov, Effect of molecular structure on combustion of polynitrogen energetic materials, Solid propellant chemistry, combustion, and motor interior ballistics, progress in astronautics and aeronautics, American Institute of Aeronautics and Astronautics, 2000, pp. 99–128.

[25] V.P. Sinditskii, V.Y. Egorshev, M.V. Berezin, G.F. Rudakov, A.V. Ladonin, D.V. Katorov, Combustion behaviour of melt-castable explosives from azetidine family, Propell. Explos. Pyrot. 33 (5) (2008) 381–389.

[26] V.P. Sinditskii, M.C. Vu, V.P. Shelaputina, A.B. Sheremetev, N.S. Alexandrova, Study on thermal decomposition and combustion of insensitive explosives 3,3′-diamino-4,4′-azofurazan (DAAzF) and 3,3′-diamino-4,4′-azoxyfurazan (DAAF), 7th International Autumn Seminar on Propellants, Explosives and Pyrotechnics, Xian, China, 7 (2007), pp. 422–428. October 23-26.

[27] A.A. Kubasov, Chemical kinetics and catalysis, part 1, textbook, Moscow State University, 2004, 143c. (in Russian, http://www.chem.msu.ru/rus/teaching/kubasov/welcome1.html).

[28] V.P. Sinditskii, L.E. Bogdanova, K.O. Kapranov, A.I. Levshenkov, V.I. Kolesov, High-energy salts of 5,5-azotetrazole. I. Thermochemistry and thermal decomposition, Fizika Gorenia I Vzryva 55 (3) (2019) 71–91 [Comb., Expl., and Shock Waves, 55(3) (2019) 308–326 (Engl. Transl.)], doi:10.15372/FGV20190309.

[29] Y.Y. Maksimov, Thermal decomposition of RDX and HMX, In Theory of Explosives, Trudy RKhTU Im. D.I. Mendeleyeva, M.: Vysshaya Shkola 53 (1967) 73–84 in Russian.

[30] V.P. Sinditskii, A.V. Bourzhava, G.F. Rudakov, D.A. Zakharova, Thermal decomposition of triazolo- and tetrazolotetrazines, Goreniye i vzryv (Comb. Explos.) 8 (2) (2015) 195–202 in Russian.

[31] V.P. Sinditskii, V.Yu. Egorshev, V.V. Serushkin, A.I. Levshenkov, M.V. Berezin, S.A. Filatov, Combustion of energetic materials governed by reactions in the condensed phase, Int. J. Ener. Mat. Chem. Prop. 9 (2) (2010) 147–192, doi:10.1615/IntJEnergeticMaterialsChemProp.v9.i2.30.

[32] V.P. Sinditskii, V.Yu. Egorshev, V.V. Serushkin, S.A. Filatov, Combustion of energetic materials controlled by condensed-phase reactions, Fizika Gorenia i Vzryva 48 (1) (2012) 89–109 [Comb. Expl. and Shock Waves, 48(1) (2012) 81-99 (Engl. Transl.)].

[33] V.P. Sinditskii, V.Y. Egorshev, V.V. Serushkin, A.I. Levshenkov, M.V. Berezin, S.A. Filatov, S.P. Smirnov, Evaluation of decomposition kinetics of energetic materials in the combustion wave, Thermochim. Acta 496 (1–2) (2009) 1–12, doi:10.1016/j.tca.2009.07.004.

[34] Y.B. Zeldovich, Theory of combustion of propellants and explosives, Zh. Eksper. Teoret. Fiziki 12 (11–12) (1942) 498–524 in Russian.

[35] V.P. Sinditskii, V.Y. Egorshev, M.V. Berezin, V.V. Serushkin, Mechanism of HMX combustion in a wide range of pressures, Fizika Gorenia I Vzryva 45 (4) (2009) 128–146 [Comb Explos and Shock Waves, 45(4) (2009) 461–477(Engl. Transl.)], doi:10.1007/s10573-009-0057-x.

[36] V.P. Sinditskii, On the nature of the burning rate-controlling reaction of energetic materials for the gas-phase model, Fizika Gorenia I Vzryva 43 (3) (2007) 59–71 [Comb Explos and Shock Waves, 43(3) (2007) 297-308 (Engl. Transl.)], doi:10.1007/s10573-007-0043-0.