THERMOCHEMICAL PROPERTIES OF MESOIONIC 1,2,3,4-OXATRIAZOLE

T. S. Kon'kova[1], E. A. Miroshnochenko[1], Yu. N. Matyushin[1], A. B. Vorob'ev[1], Ja. O. Inozemtcev[1], A. V. Inozemtcev[1], O. V. Serushkina[2], and I. L. Dalinger[2]

[1]N. N. Semenov Federal Research Center for Chemical Physics, Russian Academy of Sciences, 4 Kosygin Str., Moscow 119991, Russian Federation

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

Abstract: The combustion energies of a number of new mesoionic five-membered heterocyclic compounds of arylazasydnones and arylazasydnoimines containing donor and acceptor substituents at different positions of the phenyl ring have been experimentally determined. Calorimetric measurements of combustion energies were carried out on a precision automatic combustion calorimeter with an isothermal shell (designed by the Laboratory of Thermodynamics of Energetic Materials of the N. N. Semenov Federal Research Center for Chemical Physics, Russian Academy of Sciences), designed specifically for the combustion of energetic compounds. With a sufficiently large bomb volume (210 cm^3), the calorimeter has a low energy equivalent (550 cal/K), which makes it possible to use small amounts of energetic materials in the experiment and, thereby, reduce the risk of transition of combustion into an explosion. Based on the obtained values, the enthalpies of combustion and formation in the standard state of potentially energy-intensive nitroaryl derivatives of 1,2,3,4-oxatriazolium-5-olates and 1,2,3,4-oxatriazolium-5-aminides are calculated. The influence of the electronic properties of the aryl substituent was estimated. It was found that the contribution of the azasydnoimine fragment (B) to the enthalpy of combustion for diphenyl derivatives is −189 kcal/mol. The calculated values for the contribution of the azasydnone cycle to the enthalpy of combustion of phenylazasidnons depend on the position and nature of the substituent in benzene and, therefore, the contribution value lies in the range from −105 to −126 kcal/mol. Based on the data obtained on the enthalpies of formation of derivatives of 1,2,3,4-oxatriazoles and the values determined from them by the contributions of fragments (A) and (B), it is possible to predict the thermochemical characteristics of hypothetical compounds with azasydnone and azasydnoimine fragments.

Keywords: calorimetry; enthalpy of combustion; enthalpy of formation; azasydnone; azasydnoimine; mesoionic compounds

DOI: 10.30826/CE20130214

Table Captions

Table 1 Combustion energies of diphenyl derivatives of 1,2,3,4-oxatriazolium aminides

Table 2 Thermochemical characteristics of diphenyl derivatives with azasydnoimine fragments

Table 3 Thermochemical characteristics of phenyl-, methylphenyl-, and nitrophenyl derivatives of 1,2,3,4-oxatriazoliumolates

Acknowledgments

The reported study was funded by RFBR, project No. 16-29-01094 ofi_m, and by the subsidy given to N. N. Semenov Federal Research Center for Chemical Physics of the Russian Academy of Sciences to implement the state assignment of the topic 44.8 "Foundation studies of conversion processes of energetic materials and development of scientific grounds of controlling these processes" (Registration No. 0082-2014-0012).

References

1. Inozemtcev, Ya. O., A. B. Vorobyev, A. V. Inozemtsev, and Yu. N. Matyushin. 2014. Kalorimetriya energoemkikh soedineniy [Calorimetry of energetic materials]. *Goren. Vzryv (Mosk.) — Combustion and Explosion* 7:260–270.
2. Kon'kova, T. S., E. A. Miroshnichenko, Yu. N. Matyushin, A. B. Vorob'ev, Ya. O. Inozemtsev, I. L. Dalinger, T. K. Shkineva, and S. A. Shevelev. 2015. Energii soleobrazovaniya geterotsiklicheskikh soedineniy [Energies of salt formation for heterocycles]. *Goren. Vzryv (Mosk.) — Combustion and Explosion* 8(2):174–185.

3. Cox, J. D, D. D. Wagman, and V. A. Medvedev, eds. 1989. CODATA key values for thermodynamics. New York – Washington – Philadelphia – London. Final Report of the CODATA Task Group on Key Values for Thermodynamics.
4. Pedley, J. B. 1994. *Thermochemical data and structures of organic compounds*. College Station, TX: Thermodynamic Research Center. Vol. 1. 200 p.
5. Suntsova M. A., and O. V. Dorofeeva. 2016. Use of G4 theory for the assessment of inaccuracies in experimental enthalpies of formation of aromatic nitro compounds. *J. Chem. Eng. Data* 1:313–329.
6. Kon'kova, T. S., E. A. Miroshnichenko, Yu. N. Matyushin, A. B. Vorob'ev, Ya. O. Inozemtsev, I. L. Dalinger, T. K. Shkineva, and S. A. Shevelev. 2018. Termokhimicheskie svoystva fenilazasidnonov [Thermochemical properties of phenylazasydnones]. *Goren. Vzryv (Mosk.) — Combustion and Explosion* 11(3):125–129.

Received May 14, 2020

Contributors

Kon'kova Tatiana S. (b. 1941) — Doctor of Science in chemistry, chief research scientist, N. N. Semenov Federal Research Center for Chemical Physics of the Russian Academy of Sciences, 4 Kosygin Str., Moscow 119991, Russian Federation; taskon@mail.ru

Miroshnichenko Eugeny A. (b. 1938) — Doctor of Science in chemistry, chief research scientist, N. N. Semenov Federal Research Center for Chemical Physics of the Russian Academy of Sciences, 4 Kosygin Str., Moscow 119991, Russian Federation; eamir02@mail.ru

Matyushin Yury N. (b. 1940) — 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; professor, National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), 31 Kashirskoe Sh.,Moscow 115409, Russian Federation; ynm@polymer.chph.ras.ru

Vorob'ev Alexey B. (b. 1946) — Candidate of Science in chemistry, 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; ynm07@mail.ru

Inozemtsev Jaroslav O. (b. 1966) — 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; vectr1@yandex.ru

Inozemtsev Alexey V. (b. 1976) — research scientist, N. N. Semenov Federal Research Center for Chemical Physics of the Russian Academy of Sciences, 4 Kosygin Str.,Moscow 119991, Russian Federation; vectr1@yandex.ru

Serushkina Olga V. (b. 1964) — junior research scientist, N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky Prosp., Moscow, 119991, Russian Federation; olgvikser@rambler.ru

Dalinger Igor L. (b. 1961) — Doctor of Science in chemistry, head of laboratory, N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky Prosp., Moscow, 119991, Russian Federation; dalinger@ioc.ac.ru