

N-nitrosaccharins are not insensitive chemicals

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Nitroaromatics are essential across many industries (pharmaceuticals, explosives, agrochemicals), driving the search for inexpensive, stable and affordable nitrating agents. Recently, in this journal, Katayev et al.¹ suggested N-nitrosaccharin **1** (2-nitrobenzo[d]isothiazol-3(2H)-one 1,1-dioxide) as a useful source of nitronium ion. Later, the same group demonstrated that **1** and more nitrated relative also synthesized in ref. 1, 6,N-dinitrosaccharin **2** (2,6-dinitrobenzo[d]isothiazol-3(2H)-one 1,1-dioxide) are efficient agents in nitration of (het)aryl silanes² and *O*-nitration of alcohols and diols³. While both nitrosaccharins are undoubtedly useful chemicals, in this correspondence we want to focus the attention of its safety aspects.

The claim that **1** is shock insensitive¹ is based on two laboratory tests. The one that is more similar to standard impact sensitivity testing, was dropping of 1 kg hammer from 0.8 m height to the sample. A simple calculation gives the drop energy of 8 J supplied to the sample. It is a level of sensitivity of high brisant explosives; less powerful, but still explosive compounds are well known, for example, trinitrotoluene shows 50% explosions at hammer energy of 30 J⁴. Therefore, the lack of reaction under conditions of tests in ref. 1. does not imply the insensitivity of discussed materials.

We prepared **1** and **2** on gram-scale and evaluated their thermal and mechanical hazards using the standard dedicated approaches from chemical industry. N-nitrosaccharin **1** has impact sensitivity of 22 ± 5 J (energy corresponding to 50% of positive events, with both decompositions and explosions registered), and insensitive toward friction (no reaction at maximal friction force of 360 N). 6,N-dinitrosaccharin **2** is expectedly more sensitive, 10 ± 3 J to impact and also friction insensitive. Thermal stability of nitrosaccharins was then assessed using Yoshida equations^{5,6} with the results of sealed cells DSC experiments.

Figure 1a shows the resulting DSC signal for **1** in hermetic crucibles, and, for comparison, the DSC curve for low-confined conditions (light crucibles, pierced lids), similar to those reported in ref. 1. Note, that only about one-third part of the material is consumed in the course of the first exotherm; the remaining mass loss at low-confinement conditions is caused by the vaporization of the primary reaction products, saccharin and 2-sulfobenzoic acid cyclic anhydride (see Section S3 of Supplementary Information for details). When this vaporization is retarded (hermetic crucibles), the breakdown of semiproducts increases the total decomposition enthalpy.

The thermal hazard scale by total decomposition enthalpy puts **1** close to such known exothermic chemicals, like 1*H*-tetrazole and diethylazodicarboxylate. Dinitrosaccharin **2** evolves the amount of heat near shock sensitive⁷ formaldoxime trimer hydrochloride TFO·HCl and about half that of trinitrotoluene (Fig. 1b). When the decomposition heat is taken altogether with the onset temperature using the Pfizer modification⁶ of Yoshida equations⁵, both **1** and **2** are marked as a potentially shock sensitive (Fig. 1b), agreeing with the above experiments. In addition, we apply the recently suggested O.R.E.O.S. method⁸, to see the level of predicted hazard and its distribution over the amount of material to be handled. For all scales from <5 g to >500 g, **1** and **2** are ranked with a high hazard (Table S6, Supplementary Information). Lastly, we calculate the explosive potential of analyzed species, i.e., the amount of energy they can release if detonated. This virtual detonation velocity for mononitrated saccharin is lower than those of low explosive, but for **2** it approaches the TNT (Table S7, Supplementary Information).

In total, we show thermal and explosion hazards of two suggested nitrosaccharins, using the experimental and screening procedures

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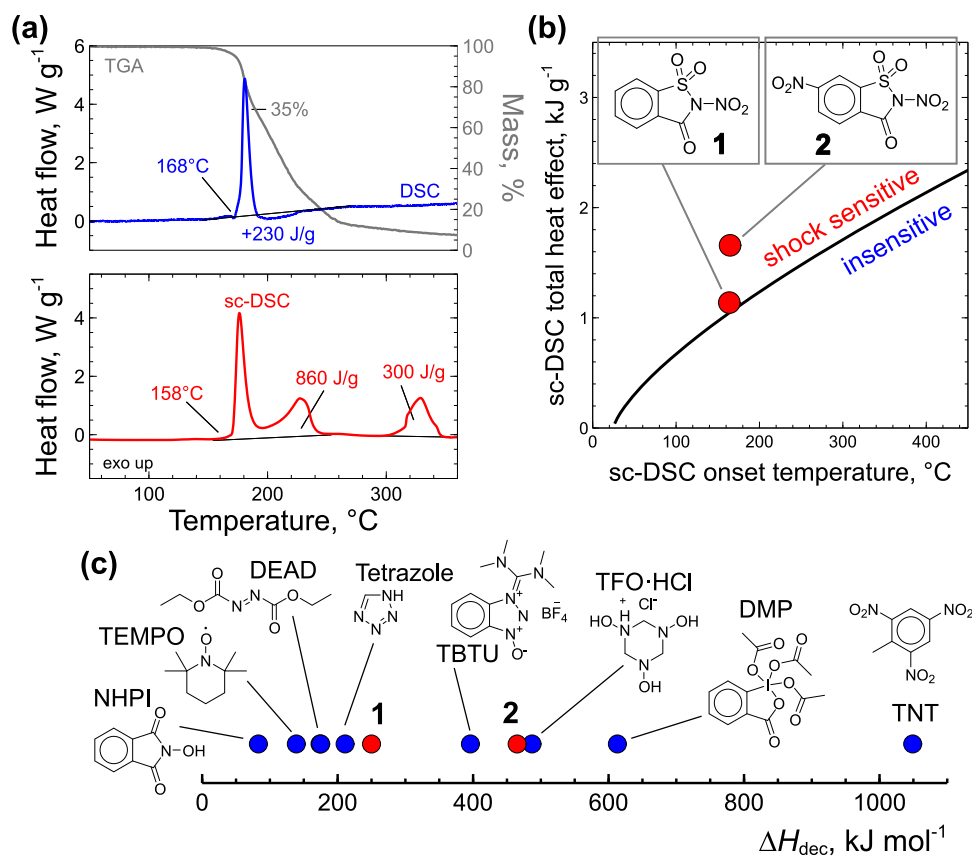


Fig. 1 | Thermal hazards of nitrosaccharins. a Calorimetry (DSC) and mass loss (TGA) signals for linearly heated **1**: the upper plot for low-confinement conditions (as in ref. 1), the bottom plot for standard chemical industry approach with hermetic crucibles (no heat lost). **b** Yoshida-type plot with our data for saccharins and

curve as suggested by Pfizer⁸ for shock sensitivity (compounds nesting above curve are potentially sensitive). **c** Decomposition enthalpy scale measured for **1**, **2** compared to some other chemicals (raw data can be found in Table S1, Supplementary Information).

from chemical industry. Evidence points to that this useful reagent should be used with care especially at medium and large scale.

Data availability

The authors declare that the data supporting the findings of this study are available within the paper and its Supplementary Information files. Should any raw data files be needed in another format, they are available from the corresponding author upon request.

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Author contributions

N.V.M. wrote the manuscript and participated in hazard assessment; I.L.D. and I.A.V. synthesized the materials. I.N.M. runs the DSC tests and thermochemical calculations.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary information The online version contains supplementary material available at <https://doi.org/10.1038/s41467-026-69702-8>.

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