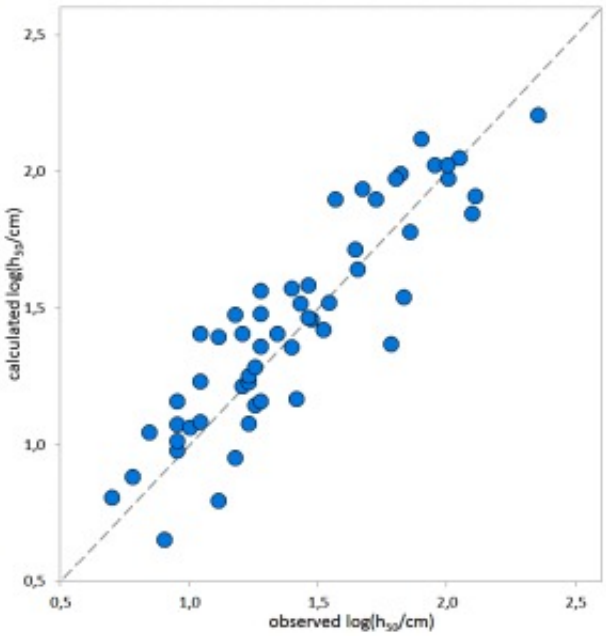
Sensitivity to explosion of chemicals estimated using only a hand held calculator



Predicted versus experimentally derived sensitivities for nitroaliphatic and nitramine compounds not used to develop the model.

The ability to predict the explosivity of energetic materials on the basis of their molecular structure would be of utmost interest for the design of explosives and propellants, to develop safe handling practices in the field and to satisfy the requirements of recent chemical substance regulations. A variety of insults may be applied to a material in order to characterize its behavior. However, the sensitivity to mechanical impact is especially relevant in practice. It is most often characterized by the height that a given weight must be dropped onto a sample to initiate an observable decomposition with a 50% probability. This property is extremely complex. First of all, it depends on the defects present in all real-life energetic materials, as experiments have revealed that single crystals are extremely difficult to detonate. Indeed, if spread uniformly into the material, the mechanical energy provided by the impacting weight would be far too low to break chemical bonds. To initiate chemical reactions, this energy must focus in specific regions, which is only possible if the sample exhibits localized defects acting as energy traps that heat up and lead to the formation of so-called hot spots. In principle, the fact that the exact nature and concentration of defects in materials are usually unknown might prevent the existence of deterministic relationships between impact sensitivity and molecular structure. The difficulty is exacerbated by the complexity of organic energetic compounds, usually made of crystal powders, and by the fact that sensitivity depends on many additional factors beyond molecular structure: material porosity, crystal morphology, particle

size, ambient humidity during measurements, actual equipment used…

Currently, sensitivity may be reduced with the help of specific treatments, generally aimed at decreasing the amount of defects in the material. Nevertheless, it is clear from decades of experience that chemical structure plays a prominent role, with some molecules clearly more sensitive than others. Therefore, extensive work has been carried out for over half a century to predict sensitivity for new compounds. Given the theoretical complexity of the problem, many empirical models were reported, using increasingly sophisticated descriptors and regression techniques. Meanwhile, few physically motivated models were described. Whatever the modeling strategy adopted, all procedures fail in demonstrating reasonable predictions for extended test sets and the problem has remained a stubborn challenge.

Progress was obtained only very recently, on the basis of the new assumption that the critical step in initiation is the propagation of the chemical decomposition process from small reactive centers to more extended regions. In this approach, the condition for initiation is that chemical energy is released sufficiently fast compared to the rate at which it is dissipated in the surroundings. Drastic approximations yield a procedure based only on the empirical formula of the compound and on approximate values for the energies of its weakest chemical bonds. It allows one to estimate impact sensitivity for most explosives on the basis of a simple equation involving only three adjustable parameters.

It may seem paradoxical that, in spite of its complexity, impact sensitivity is predictable with such a simple model. This finding implies that despite their critical role, defects modify sensitivity values in the same way for most explosives. Moreover, they confirm that molecular structure is the main determinant of sensitivity. Finally, they question the significance of alternative factors that were put forward to explain sensitivity values for specific materials.

Publication

Impact sensitivities of energetic materials: Exploring the limitations of a model based only on structural formulas.
Mathieu D, Alaime T
J Mol Graph Model. 2015 Sep 7