

SUPPORTING INFORMATION

Impact sensitivities of energetic materials derived from easy-to-compute *ab initio* rate constants

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1 Data set details

The present data are mostly taken from a database of sensitivities measured according to the so-called ERL Type 12 procedure, taken from an earlier compilation¹ from which salts were removed and to which additional values measured according to the same standard were collected from original research papers². Some errors in this data set were subsequently corrected and duplicates removed^{3,4}.

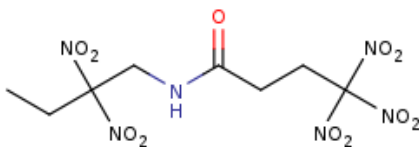
In this work, we used the training set of Keshavarz⁵, which is mainly a subset of the one mentioned above, except that it also include a couple of salts and a new duplicate, namely *N,N'*-dinitro-1,2-ethanediamine. The corresponding training set is very small, with only eight entries, including a salt (ammonium 5-nitrotetrazolate) and three drop weight impact heights which were not reported to be obtained according to the same ERL Type 12 procedure. Therefore, this test set is only used in this work to check that the present implementation of the Keshavarz approach, referred to as Mod-K, is consistent with the performance of the original one.

For a more in-depth comparison of the various estimation methods considered, we use a large external test set made of all ERL Type 12 data at hand that were not included in the Keshavarz data sets. We discard all duplicates on the basis of their canonical SMILES generated using the RDKit library⁶. Salts are removed as well since there are in very small number. The resulting training and test sets are compiled in Table S3.

2 Keshavarz approach

As an additional comparison of the present approach to previous ones, in addition to those previously reported^{2,7,8}, we initially planned to implement and test exactly the same model as reported by Keshavarz⁵. Despite the fact that textual descriptions in research papers are ill-suited to accurately describe such convoluted models, we could easily reproduce earlier procedures based on this approach to estimate spark sensitivity of nitroarenes³ or friction sensitivity⁹. However, this prove not possible for the model reported in Ref.⁵. This is because the estimated sensitivities reported in this paper are not consistent with the rules described, which comes as no surprise as the latter are specially intricate.

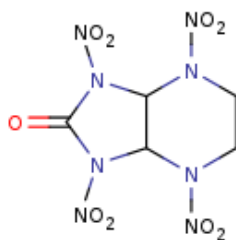
This may be simply illustrated using 2,2-dinitrobutyl-4,4,4-trinitrobutyramide (CAS number 71706-43-9) as an example. This molecule is shown below:



With $C_8H_{12}N_6O_{11}$ as empirical formula and a molecular weight of 368 g/mol, a core estimate of $\log(h_{50})$ is obtained as follows according to Eq. 4 in Ref. 5:

$$\log(h_{50})_{\text{core}} = -0.584 + (61.62 \times 8 + 21.53 \times 12 + 27.96 \times 6)/368 = 1.91 \quad (1)$$

An estimated h_{50} value of 59 cm is reported for this compound, which corresponds to $\log(h_{50}) = 1.77$. Therefore, a non-zero correcting function F^- must be used to decrease the core value of $\log(h_{50})$ from 1.91 down to the reported value of 1.77. However, none of the F^- corrections compiled in Table 2 in Ref. 5 applies to this molecule. Therefore, some additional information is missing so that we can reproduce the data reported in Table 1 of this paper. An inverse problem is observed for 2,5,7,9-tetranitro-2,5,7,9-tetraazabicyclo[4.3.0]nonane-8-one, i.e. the following nitramine:



With $\text{C}_5\text{H}_6\text{N}_8\text{O}_9$ as empirical formula and a molecular weight of 322 g/mol, a core estimate of $\log(h_{50})$ is obtained as follows according to Eq. 4 in Ref. 5:

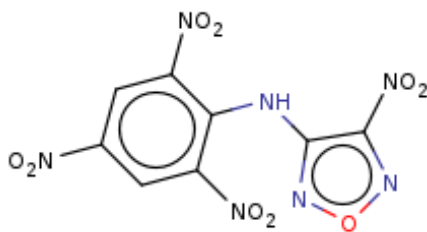
$$\log(h_{50})_{\text{core}} = -0.584 + (61.62 \times 5 + 21.53 \times 6 + 27.96 \times 8)/322 = 1.47 \quad (2)$$

On the other hand, Ref. 5 reports an estimated value h_{50} value of 44 cm for this compound, which corresponds to $\log(h_{50}) = 1.64$. Therefore, it may be realized that a correction $F^+ = 0.65$ would be required to reproduce the estimated value. Although the rules defining F^+ are specially intricate, there seems to be no way to justify such a correction from the rules reported in Ref. 5.

Nevertheless, it might be interesting to estimate the potential of such an approach, although it is clear that it is prone to fail for any structure for which unanticipated corrections F^+ and F^- are required, and leads to ambiguities whenever several conditions requiring corrections arise simultaneously^{3,9}. To this goal, we consider a simplified version referred to as Mod-K. This variant was obtained through some simplification of the rules described in Ref. 5. Rather than attempting a comprehensive description of the underlying rules, we provide an implementation of this model in the attached script Mod-K.py.

3 Mod-7P and Mod-2P models: worked-out examples

Although the models detailed in the article are very simple and require only back-of-the-envelope calculations, we detail here the evaluation of $\log(h_{50})$ using Mod-7P and Mod-2P, so as to emphasize the differences between the two models. For this example, 3-nitro-4-picrylamino-furazan is selected as a test case:



This molecule with $N_A = 27$ atoms is especially poorly estimated using both models. Applying the H_2OCO_2 arbitrary to the empirical formula $\text{C}_8\text{H}_3\text{N}_7\text{O}_9$ yields as decomposition products:

$$(3/2) \text{H}_2\text{O} + (15/4) \text{CO}_2 + \dots \text{ species with zero as formation enthalpy (solid carbon and dinitrogen)}$$

Using the value of -142.5 kJ/mol for the solid-state heat of formation, estimated using simple additivity schemes^{10,11}, along with the reference experimental values of -241.8 kJ/mol for H_2O and -393.5 kJ/mol for CO_2 , the energy content of the explosive is obtained in kJ/mol as follows:

$$E_c = (-242.5) - [(-3/2) \times (-241.8) + (15/4) \times (-393.5)] = 1696 \quad (3)$$

At this stage, Mod-7P and Mod-2P diverge in both the evaluation of the effective temperature $k_B T$ (in kJ/mol) and the definition of the explosiveshores. For Mod-7P:

$$k_B T = \eta \frac{E_c}{3N_A/2} = 30.3 \times \frac{1696}{3 \times 27/2} = 1269 \quad (4)$$

whereas the effective temperature for Mod-2P is simply:

$$k_B T = \frac{E_c}{3/2} = \frac{1696}{3/2} = 1130 \quad (5)$$

Mod-7P model

Mod-7P identifies five decomposition paths associated with the five potential explosiveshores detected on the molecule, with corresponding activation energies in kJ/mol as follows:

- 3 aromatic nitro groups on benzene ring: $E^\ddagger/(\text{kJ}\cdot\text{mol}^{-1}) = 221$
- 1 aromatic nitro group ortho to NH on furazan ring: $E^\ddagger/(\text{kJ}\cdot\text{mol}^{-1}) = 67$
- 1 furazan ring: $E^\ddagger/(\text{kJ}\cdot\text{mol}^{-1}) = 426$

These data are taken from Table S1 for precalculated C–NO₂ bond dissociation energies, and in Table 1 for the fitted activation energy associated with the last reaction path, involving the decomposition of the furazan ring.

The prefactors associated to these five decomposition pathways are all assumed to be equal to that associated with homolytic C–NO₂ dissociation. Therefore, the relative rate constant scaled by the $k(\text{C–NO}_2)$ value is obtained as:

$$k = \frac{1}{27} \left(3 \times \exp\left(-\frac{221}{1269}\right) + 1 \times \exp\left(-\frac{67}{1269}\right) + 1 \times \exp\left(-\frac{426}{1269}\right) \right) = 0.154 \quad (6)$$

Finally, using the Mod-7P parameters $n = 4$ and $k_c = 0.36$ reported in Table 1:

$$h_{50}/\text{cm} = \left(\frac{0.36}{0.154}\right)^4 \quad \text{and} \quad \log(h_{50}) = 1.48 \quad (7)$$

Mod-2P model

In contrast to Mod-5P, Mod-2P identifies six decomposition paths. This is because two decomposition paths are considered, corresponding to the breaking of one or the other of the NO bonds of the furazan ring. The activation energies of those six paths are:

- 3 aromatic nitro groups on benzene ring: $E^\ddagger/(\text{kJ}\cdot\text{mol}^{-1}) = 221$
- 1 aromatic nitro group ortho to NH on furazan ring: $E^\ddagger/(\text{kJ}\cdot\text{mol}^{-1}) = 67$
- 2 N–O bonds in furazan ring: $E^\ddagger/(\text{kJ}\cdot\text{mol}^{-1}) = 139$

These data are all precalculated on model compounds and are compiled in Table S1. In contrast to Mod-7P, none of them was fitted against experiment.

Another major difference with respect to Mod-7P is the fact that all prefactors are calculated independently, rather than fitted. According to the resulting values compiled in Fig. 4, the prefactors associated with the three different kinds of reactions listed above are all 845 cm⁻¹, except for the cleavage of N–O bonds in the furazan rings for which the prefactor is 1159 cm⁻¹. Hence the following expression for the rate constant in cm⁻¹:

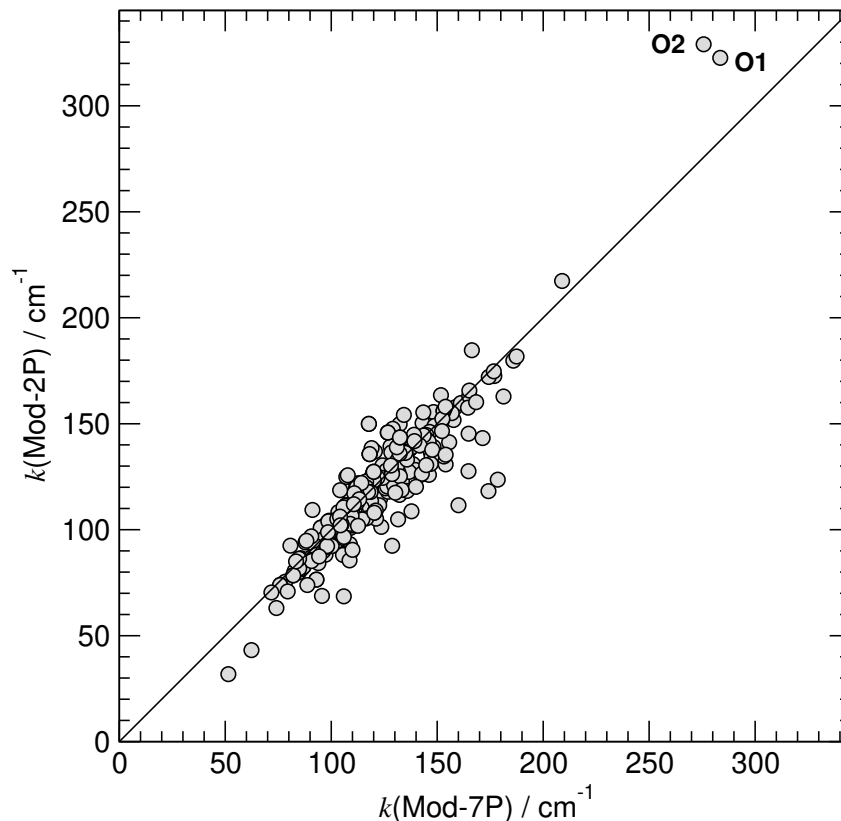
$$k = \frac{1}{27} \left(3 \times 845 \times \exp\left(-\frac{221}{1130}\right) + 1 \times 845 \times \exp\left(-\frac{67}{1130}\right) + 2 \times 1159 \times \exp\left(-\frac{139}{1130}\right) \right) = 182.6 \quad (8)$$

Finally, using the Mod-2P parameters $n = 7/2$ and $k_c = 0.41 \times 845 \text{ cm}^{-1}$ reported in Table 1:

$$h_{50}/\text{cm} = \left(\frac{0.41 \times 845}{183}\right)^4 \quad \text{and} \quad \log(h_{50}) = 0.98 \quad (9)$$

4 Comparison of Mod-7P and Mod-2P decomposition rates

The changes observed in the ranking of impact sensitivities on going from Mod-7P to Mod-2P clearly reflects differences in calculated values of the reaction rate k , for which the values calculated by the two methods for the whole dataset are compared in the figure below:



Despite a strong correlation between both sets of values ($R^2 = 0.80$), substantial differences are observed, especially for nitric esters for which systematically lower rates are obtained on going from Mod-7P to Mod-2P. Interestingly, both models predict specially large k -values for the four nitrofurazans (particularly O1 and O2) that are predicted much too sensitive by Mod-2P.

References

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