

Supporting Information

Sensitivity of energetic materials: theoretical relationships to detonation performance and molecular structure

Didier Mathieu

CEA, DAM, Le Ripault, 37260 Monts (France)

E-mail: didier.mathieu@cea.fr

Phone: +33-02-47-34-41-85

S1. Procedure employed to evaluate gas-phase enthalpies of formation

Current reliable and versatile approaches to the prediction of formation enthalpies rely on quantum chemical calculations. Focusing on practical methods applicable to molecules with up to 50 atoms, a popular model especially well-suited to energetic materials is the one developed by Rice and Byrd, according to which $\Delta_f H_{gas}^0$ is obtained as the sum of the total electronic energy and additive atom and group equivalents [1]. However, some experimental values used to train this model were subsequently revised, as pointed out recently by Elioﬀ et al. [2]. Therefore, although it is very similar to the Byrd and Rice procedure, the present one is fitted against the experimental data compiled by Elioﬀ et al. as they integrate recent revisions.

Another issue stems from the fact this dataset includes only 45 CHNO compounds, while some explosives from the present h_{50} database exhibit F and Cl atoms as well. Therefore, the present $\Delta_f H_{gas}^0$ data set is extended by including 17 fluorinated and chlorinated compounds for which gas-phase enthalpies are available from the NIST Webbook database [3]. These compounds and corresponding data are compiled in Table S3 in the Excel file provided as Supporting Information.

On the other hand, in order to ensure that anybody can apply the present procedure, including people who do not own a license for a commercial computer code, our calculations are based on efficient density functional theory (DFT) schemes implemented in the freely available ORCA package [4].

More specifically, the molecule is optimized using the BP86 density functional associated with the DefBas-1 ORCA default basis set [5] and the resolution of the identity (RI) approximation [6]. The latter allows for fast computations despite the fairly large basis set. This level of theory is promoted by the ORCA developers and specified by the keyword "Quick-Opt" in the input file. The total electronic energy E_{elec} is then obtained from a single-point calculation at the B3LYP level using the DefBas-4 basis set, according to a standard ORCA procedure referred to by the "DFT-Energy" keyword in the input file [5].

Finally, our procedure is based on more reliable reference data and more accurate DFT energies compared to the 2006 original scheme [1]. As a result, the group equivalents previously employed prove unnecessary, except for O–NO₂ groups. Indeed, for the Byrd and Rice CHNO data set, and in spite of the reduced number of adjustable parameters employed, we obtain results very similar to those reported for the original procedure, with a root mean square error (RMSE) of 12.4 kJ/mol (12.1 kJ/mol for the earlier scheme) and a maximum error of 39.2 kJ/mol (against 38.1 kJ/mol previously). Therefore, the procedure was eventually fitted against all 62 compounds in the extended data set. The final parameters thus obtained are reported in Table S1.

Table S1: Atom or group equivalent energies ϵ (kJ/mol) with associated standard deviations σ (kJ/mol) and corresponding numbers of training set entries N_{occ} .

	ϵ	σ	N_{occ}
H	1557.9	1.5	53
C	100040.3	2.8	46
C'	100053.4	1.3	25
N	143780.6	3.3	42
N'	143780.1	1.6	18
O	197320.7	5.1	12
O'	197327.1	2.0	49
F	261937.1	1.8	10
Cl	1208093.7	2.8	7
O-NO ₂	21.7	6.3	4

S2. Estimating impact sensitivity: worked out examples for FOX-7 and DNPP explosives

The evaluation of sensitivity data (h_{50}) from molecular structure using the present model is demonstrated here for two explosives recently considered by other authors [7], namely FOX-7 and DNPP.

This model described in full detail elsewhere [8] is very straightforward as it relies on extremely simple equations, namely:

$$h_{50} = \left(\frac{k_c}{k_{pr}} \right)^4 \quad (1)$$

$$k_{pr} = \frac{1}{N_A} \sum_i Z_i \exp \left(- \frac{E_i^\ddagger}{k_B T_e} \right) \quad (2)$$

$$k_B T_e = \eta \frac{E_c}{3N_A/2} \quad (3)$$

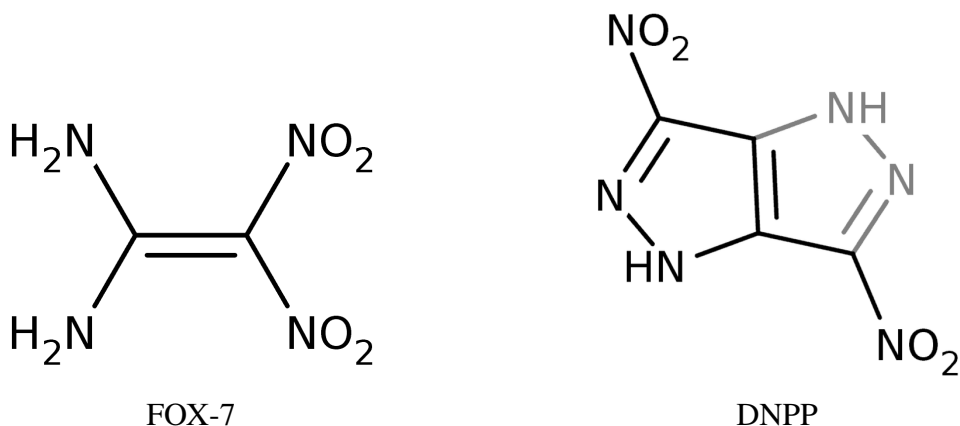


Figure S1: Molecular structures of FOX-7 and DNPP.

The procedure involves two dimensionless empirical constants: $k_c = 0.342$ and $\eta = 16.5$. To apply this model to an arbitrary compound, the following input data is needed:

- The activation energies and prefactors associated with every possible decomposition pathway: E_i^\ddagger and Z_i
- The total chemical energy content evaluated on the basis of the $\text{H}_2\text{O}-\text{CO}_2$ arbitrary: E_c
- The total number of atoms per formula unit: N_A

Activation energies and prefactors

In view of their relatively minor role compared to activation energies, all prefactors Z_i are assumed to be unity. Alternative values $Z_N = 1.42$ and $Z_O = 1.36$ employed for $\text{N}-\text{NO}_2$ and $\text{O}-\text{NO}_2$ homolytic bond scissions [8] are irrelevant for the FOX-7 and DNPP.

The actual values employed for activation energies E_i^\ddagger play a more critical role. To make the model applicable to a wide range of compounds while avoiding the need for quantum chemical computations, standard E_i^\ddagger values computed on model systems on the basis of B3LYP/def2-TZVP//HF/3-21G calculations, using the standard scaling factor of 0.9207 for vibrational energies, have been tabulated [8, 9]. Here, we demonstrate the application of this model to molecules for which reliable standard activation energies are not available from these tables.

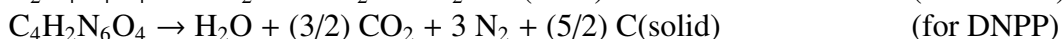
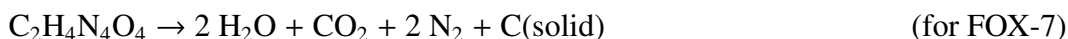
As shown on Fig. S1, the two nitro groups in FOX-7 exhibit an unique environment. Therefore, it might be daring to use a standard value for the corresponding bond dissociation energy (BDE), like the value of 216 kJ/mol obtained for 3-Nitro-1,2,4-triazole-5-one [8]. Therefore, the $\text{C}-\text{NO}_2$ bond dissociation energy for the nitro groups in FOX-7 is presently computed using the above-mentioned computational procedure, leading to a relatively high value of 274.2 kJ/mol.

For DNPP, standard activation energies cannot be used because the decomposition pathway initiated by the transfer of a proton toward an oxygen atom is associated with an energetic barrier of 162.8 kJ/mol, far lower than the $\text{C}-\text{NO}_2$ bond dissociation energy of 232.4 kJ/mol obtained from the energy difference between isolated radical products and the initial unreacted molecule.

Finally, the activation energies obtained using the usual computational procedure previously employed to fit the present model are 274.2 kJ/mol for FOX-7 and 162.8 kJ/mol for DNPP.

Chemical energy content

The total chemical energy content E_c is obtained from the following decomposition reactions:



Using experimental values compiled in the NIST Chemistry Webbook [3] for the formation enthalpies of the decomposition products, we obtain from these equations the following values of E_c :

- 874 kJ/mol for FOX-7
- 832 kJ/mol for DNPP

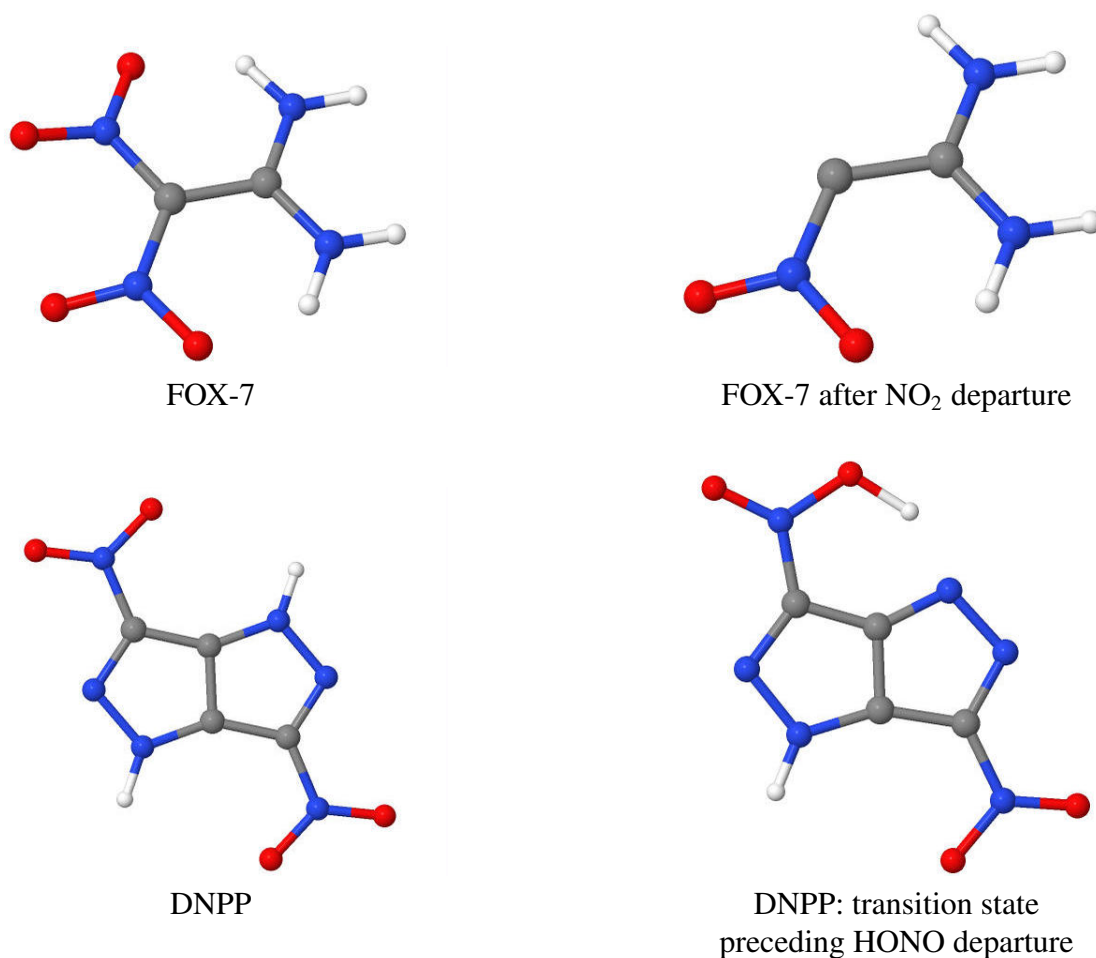


Figure S2: Molecular geometries involved in the evaluation of activation energies for the decomposition of FOX-7 and DNPP.

These values are obtained neglecting the formation enthalpies of the unreacted explosives, for which reliable and well-established experimental data are still lacking. Up to now, solid-state formation enthalpies were recently reported to be -134 kJ/mol for FOX-7 and about 272-323 kJ/mol for DNPP [10].

Numbers of atoms

The numbers of atoms are $N_A = 14$ for FOX-7 (C₂H₄N₄O₄) and $N_A = 16$ for DNPP (C₄H₂N₆O₄).

Evaluation of impact sensitivities

It is now straightforward to calculate h_{50} using equations 1-3, $Z_i = 1$ and values of E_i^\ddagger , E_c and N_A derived above. This is detailed below for FOX-7 and DNPP.

FOX-7

$$k_B T_e = 16.5 \times \frac{874}{3 \times 14/2} = 687 \text{ kJ/mol} \quad (4)$$

$$k_{pr} = \frac{2}{14} \exp\left(-\frac{274.2}{687}\right) = 0.0958 \quad (5)$$

$$h_{50} = \left(\frac{0.342}{0.0958}\right)^4 = 162 \text{ cm} \quad (6)$$

DNPP

$$k_B T_e = 16.5 \times \frac{832}{3 \times 16/2} = 572 \text{ kJ/mol} \quad (7)$$

$$k_{pr} = \frac{2}{16} \exp\left(-\frac{162.8}{572}\right) = 0.0940 \quad (8)$$

$$h_{50} = \left(\frac{0.342}{0.0940}\right)^4 = 175 \text{ cm} \quad (9)$$

References

- [1] Byrd, E. F. C.; Rice, B. M. *J. Phys. Chem. A* **2006**, *110*, 1005–1013.
- [2] Elioﬀ, M. S.; Hoy, J.; Bumpus, J. A. *Adv. Phys. Chem.* **2016**, *2016*, Article ID 5082084, 11 pages.
- [3] Linstrom, P. J., Mallard, W. G., Eds. *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*; National Institute of Standard and Technology: Gaithersburg, MD, <http://webbook.nist.gov>, 2011.
- [4] Neese, F. *WIREs: Comput. Mol. Sci.* **2012**, *2*, 73–78.
- [5] Neese, F.; Wennmohs, F. ORCA, An ab initio, DFT and semiempirical SCF-MO package, Version 3.03.3. Max-Planck-Institute for Chemical Energy Conversion: Stiftstr. 34-36, 45470 Mülheim a. d. Ruhr, Germany.
- [6] Vahtras, O.; Almlöf, J. *Chem. Phys. Lett.* **1993**, *213*, 514–518.
- [7] Politzer, P.; Murray, J. S. *J. Mol. Model.* **2014**, *20*, 2223.
- [8] Mathieu, D.; Alaime, T. *J. Mol. Graph. Model.* **2015**, *62*, 81–86.
- [9] Mathieu, D.; Alaime, T. *J. Phys. Chem. A* **2014**, *118*, 9720–9726.
- [10] Klapötke, T. M.; Witkowski, T. G. *Propel. Explos. Pyrotech.* **2016**, *41*, 470–483.