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TOWARDS A THEORETICAL DESCRIPTION OF ENERGETIC MATERIALS SENSITIVITIES

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Abstract

New ways in which the sensitivity of energetic materials can be described are presented. Particularly, a physically justified global multi-scale approach is discussed. Starting from the local decomposition kinetics through the macroscopic dynamics, this leads to the establishment of explicit expressions between microscopic and macroscopic quantities. This review outlines all the steps that lead to the physical definition of sensitivity criteria.

1 Introduction

Energetic materials are a well-known chemical family. It consists of compounds with a high energy content, stored in chemical form, which can be released in a relatively short time. They include explosives, pyrotechnic compositions, propellants and fuels. Because of their special characteristics, these materials are highly valued in the aerospace and military fields. It is therefore not uncommon to find them at the heart of the projects of the concerned institutes, whether in improvement or innovation processes.

To quantify the value of an energetic molecule, performance (propulsion, detonation) and stability criteria are needed. These criteria are particularly important regarding the synthesis of new molecules as handling is risky and unintentional initiation can have disastrous consequences. To this end, there are many experimental protocols for quantifying sensitivities that are applied. These meet clearly stipu-

lated standards, such as the STANAG agreement for NATO. In practice, several sensitivity criteria are used to distinguish the nature of the applied stress. As a result, we differentiate the impact sensitivity (mechanical, STANAG 4489), the shock sensitivity (mechanical, STANAG 4488), the friction sensitivity (mechanical, STANAG 4487), the thermal sensitivity (thermal, STANAG 4515) and the electrostatic sensitivity (radiative, STANAG 4239).

However, the use of experimental processes requires that the molecule of interest is already synthesised in sufficient quantity. Modelling appeared to be an appropriate and complementary tool that can be used to predict experimental quantities, bypassing the most costly experimental part. In this area, the literature is quite rich with a large number of approaches proposed. Firstly, there are many models based on structure-property relationships [1]. Secondly, there are models based on simulations/quantum chemistry calculations from which quantities are extracted and correlated to sensitivities [2]. Finally, simulations that seek to reproduce experiments or related phenomena are used [3][4][5].

The literature on the subject, therefore, appears to be quite vast, with notable heterogeneity. However, especially with the rise of machine learning, the field is mainly occupied by QSPR (Quantitative Structure-Properties Relationships) models whose chosen molecular descriptors only minimize a statistical error on a specific database. The derived relationships are generally not homogeneous to the predicted quantity. Note that these models must be applied to structures very similar to those used for training which is not their main purpose [6]. However, to understand in more detail the physicochemical phenomena involved, and to achieve more general and robust predictive models, it is necessary to avoid too much empiricism. In line with previous work seeking to model sensitivities based on physically justified considerations, we propose the description of a multi-scale approach to describe the global behaviour of an energetic material under stress. The multi-scale character was envisaged so that the initial macroscopic stress is first dissipated in thermal form within the material. Afterwards, it becomes available microscopically where decomposition reaction mechanisms can be triggered.

2 Preliminaries

In all generality, sensitivity can be understood as a physicochemical interplay of a large number of factors

operating at different scales. This fact is noteworthy as the literature shows that a very wide range of quantities can be correlated with sensitivity. However, as decomposition occurs at the molecular level, it is obvious that the reaction mechanisms and associated kinetics must be relevant in the equation [7]. In particular, among the first hypotheses formulated to explain sensitivity "with the hands", the dissociation energies of the R-NO₂ bonds according to their close environment were used by RICE AND AL. [8]. This finding was somehow reflected in the correlations involving the chemical reactivity of molecules. Specifically, it has been illustrated in cases where the decomposition rate, determined semi-empirically from thermo-kinetic quantities, is correlated with sensitivity [9][10]. When studying energetic molecules, the notion of so-called *explosophorous groups* comes up regularly: there are chemical groups (such as NO₂ or N₃⁺) that are supposed to be responsible for the reactivity. These chemical groups are attached to the main structure by supposedly weak bonds (C-N, N-N, O-N or even O-O): their homolytic dissociation yields highly reactive radicals with the potential to start a sustained decomposition process. By searching for the set of explosophoric groups in a molecule and determining an associated decomposition rate, a correlation with impact sensitivity was found. MATHIEU AND AL. showed that there was a correlation between this rate and the sensitivity to impact [11], as illustrated by Figure 2.1.

$$\underbrace{h_{50}}_{\text{impact sensitivity}} \quad (\text{cm}) = \left(\frac{\overbrace{k_c}^{\text{normalization factor}}}{\underbrace{k_{pr}}_{\text{reaction rate}}} \right)^4 \quad (2.1)$$

As illustrated by expression 2.1, kinetic parameters play a major role. The implicit assumption here is that it is the propagation of decomposition within the material that governs sensitivity and not the primary initiation itself. Explosophores other than nitro groups are assumed to initiate the decomposition according to specific mechanisms whose activation energies are fitted against experiment rather than computed on the basis of an assumed reaction pathway. However, some molecules that do not fall under this scheme, notably 1-picryl-1,2,3-triazole and 1-picrylbenzotriazole whose mechanisms seem to be different [12]. Understanding why and how to address this is the starting point of our study. While replacing some empirical parameters with physical ones in expression 2.1 improves its robustness, additional reaction mechanisms are needed to correct the two pathological points.

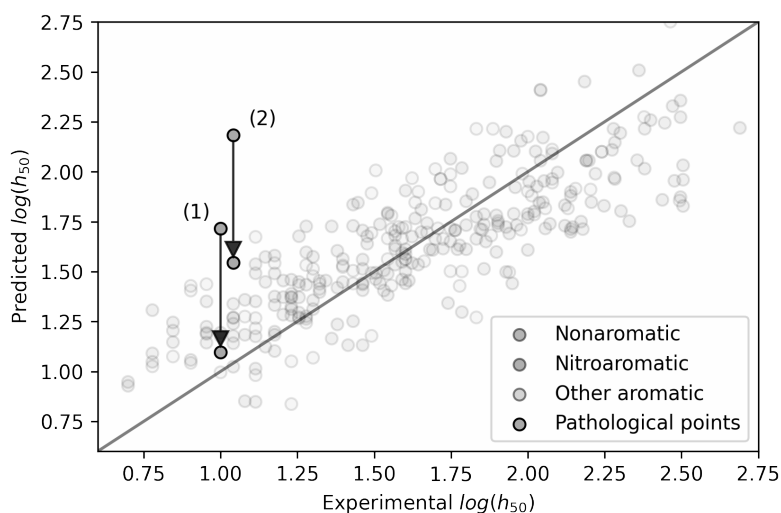


Figure 2.1. Results [11] are presented on a logarithmic scale. Predicted h_{50} (y-axis) are plotted against experimental h_{50} (x-axis). Taking into account specific mechanisms for (1) 1-picryl-12,3-triazole and (2) 1-picrylbenzotriazole allows them to be corrected.

3 Reaction mechanisms and kinetics

First of all, many studies in the literature have pointed out the diversity of reaction mechanisms even within the restricted family of energetic materials [13]. The exhaustive search for reaction mechanisms is in practice impossible even for molecules of a reasonable size because of the combinatorial explosion of the number of possible reactions [14]. However, it is possible to bias this research by looking only at the most likely reactions. As the first reactions are usually endothermic, the potential barrier recrossing (from products to reagents) probability is non-negligible. As a result, the idea was then to look only for reactions that minimize the sum of the activation energy E^\ddagger and the reaction energy $\Delta_r E$. This search bypasses a very large part of the exploration and can be terminated when the reaction path becomes exothermic. The application of this procedure to the two previous pathological points shown that the most favourable mechanisms modeled were not NO_2 departures, as illustrated in Figures 3.1 and 3.2.

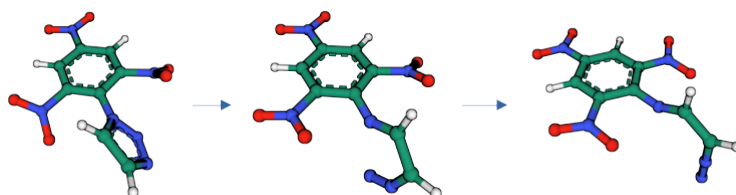


Figure 3.1. Most favorable mechanism modeled for 1-picryl-1,2,3-triazole. As shown, triazole-cycle breaking has a much lower activation energy than NO_2 departure and is therefore preferred as primary decomposition reaction.

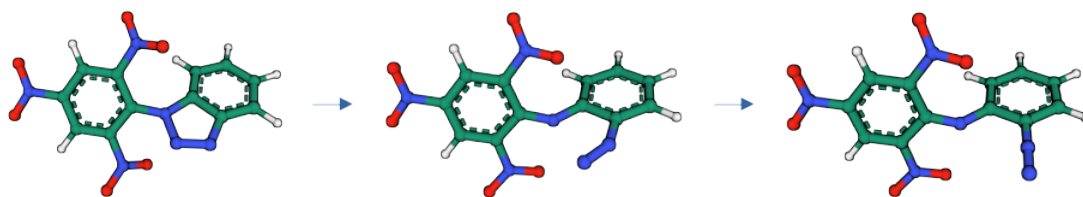


Figure 3.2. Most favorable mechanism modeled for 1-picryl-benzotriazole. As above, triazole-cycle breaking has a much lower activation energy than NO_2 departure and is therefore preferred as primary decomposition reaction.

The importance of other mechanisms such as hydrogen transfer has been highlighted by some studies [15], reinforcing the need to explore the reaction space more exhaustively beyond a supposedly "limiting" first step. In practical cases, decomposition pathways do not consist of a single step, and it is necessary to consider several before arriving at exothermic reactions (which are then no longer necessary to consider). In this case, effective kinetics appears as a composition of the kinetics of the different reactions [16].

To determine the mechanisms of the studied molecules, an automated algorithm was designed based on semi-empirical GFN-xTB functionals recently developed by GRIMME ET AL. [17]. The reaction space was explored by stretching and relaxing the structure in all its degrees of freedom. During bond stretching, the highest energy structure (if it exists) was assumed to be close to a transition state which is then optimised. By selecting at each step the reaction that minimizes the activation energy and the reaction energy, a reaction path (assumed to be the most probable) was quickly obtained even for medium to large molecules. This way, plausible reaction mechanisms were quickly accessible.

While the search for mechanisms is (numerically) expensive, it is fundamentally uncomplicated and relies simply on the exploration of a potential energy surface (admittedly of imposing dimensionality) and there are already automated algorithms in the literature (as RMG [18] or AutoMeKin [19]). As if this was not enough, the extraction of kinetic constants from these mechanisms comes with its complexity, and there is still much progress to be made in this area [20]. Harmonic Transition State Theory (HTST), stated by expression 3.1 –simultaneously developed by Eyring, Evans and Polanyi in 1935– is still largely used [21].

$$k_{\text{mHTST}} = \underbrace{\kappa}_{\text{transmission coefficient}} \cdot \underbrace{\frac{k_B T}{h} e^{\Delta S^\ddagger / k_B}}_{\text{jump rate}} \cdot \underbrace{e^{-\beta \Delta E^\ddagger}}_{\text{jump probability}} \quad (3.1)$$

In practice, HTST is improved by introducing a transmission coefficient κ which accounts for other phenomena than jumping from reagents to transition states, such as recrossing effects or tunnelling [22]. Meanwhile, some criticisms (poorly justified) were addressed to expression 3.1 as it is supposed to be a (semi-)classical theory which explicitly uses Planck constant h [23]. Particularly, the factor $k_B T / h$ is obtained by considering that the imaginary mode corresponds to a highly stretched (almost translational) mode with $\nu^\ddagger \rightarrow 0$. In this limit, the associated partition function is simply $k_B T / h \nu^\ddagger$. The whole is multiplied by ν^\ddagger which is supposed to represent the reactional frequency. Recalling that the frequencies are derived from the Gaussian curvature of the surface, the imaginary frequency simply describes the negative curvature of the potential energy surface in the reaction direction at the transition state. All these considerations are discussed in more detail by BARON [24].

4 Decomposition kinetics under thermal stress

As outlined in sections 2 and 3, reaction mechanisms are necessary to describe the decomposition kinetics of energetic materials. However, these are usually determined from experimental and, by extension, macroscopic measurements. Strictly speaking, a chemical reaction is a non-Markovian stochastic process as chemical species exchange and store internal energy over time. The reaction frequencies are therefore dependent on the history of the system and are not described by Markov processes [25]. Without going into the details, the surrounding decomposition can completely change the local kinetics.

To move away from the locality of the decomposition, described only by the local reaction kinetics, it is necessary to model the propagation of thermal stresses within the system. At the microscopic scale, the temperature is described by a fluctuating thermal bath. It is represented by a random Gaussian variable $\{\omega(t, x)\}_{t \geq 0, x \geq 0}$ with mean function $\langle \omega \rangle(t, x) = u(t, x)$ and whose two-points function is assimilated to the Dirac function in the limit of infinitesimal auto-correlation times.

A stochastic equation for the thermal fluctuations within the system was then derivable. However, it is more interesting to average out these thermal fluctuations and look at the average microscopic dynamics. The model system equation 4.1 must describe internal dissipation, exchange with an external bath u_∞ and internal energy production. In particular, the production term is described by a random variable

$\{\eta(t)\}_{t \geq 0}$. For simplicity, only a temporal correlation is considered.

$$\underbrace{\rho C_{p,m} \frac{\partial}{\partial t} u(t,x)}_{\text{evolution}} = \underbrace{\lambda \nabla^2 u(t,x)}_{\text{dissipation}} + \underbrace{\delta_{\partial\Omega} \int_{\partial\Omega} r(\omega)(u_{\infty}(t,\omega) - u(t,\omega)) d\omega}_{\text{exchange}} + \underbrace{Q \frac{\partial}{\partial t} \eta(t)}_{\text{production}} \quad (4.1)$$

Where ρ refers to the volumic density (in kg/m³), $C_{p,m}$ the specific heat capacity (in J/kg·K), λ the thermal conductivity (in W/m·K), $r(\omega)$ the exchange coefficient between the system and the environment at the position ω on the surface $\partial\Omega$ (in s⁻¹), Q the total volumic energy released during complete decomposition (in J/m³). Knowing that this random variable must describe the decomposition state of the system, and by extension the associated released energy, its cumulative distribution function is identified with the complete decomposition probability of the system. The decomposition probability is then simply described from the average decomposition kinetics and the decomposed population, as described by the expression 4.2.

$$F_{\eta}(t) := 1 - \exp\left(-\int_{-\infty}^t k(t') dt'\right) \quad (4.2)$$

By taking the derivative of this expression, multiplying it by the reaction rate and integrating it, a history-dependent effective rate $\langle k \rangle$ is derived. More precisely, $\langle k \rangle$ refers to the expected rate constant, i.e. obtained when averaging a large number of events. As a result, this quantity describes global phenomena, far from the description in expression 4.1. If one wishes to describe the system more globally, one possibility is to describe its average dynamics, by integrating over its entire spatial domain Ω . By introducing the average temperature $\langle u \rangle_{\Omega}$, equation 4.1 is transformed into 4.3.

$$\rho C_{p,m} \frac{\partial}{\partial t} \langle u \rangle_{\Omega} = \underbrace{\frac{\lambda}{L} (r_L u_{\infty;L} - r_0 u_{\infty;0})}_{\text{dissipation}} + \underbrace{\frac{1}{L} \int_{\partial\Omega} r(\omega)(u_{\infty}(t,\omega) - \langle u \rangle_{\Omega}) d\omega}_{\text{exchange}} + \underbrace{Q \langle k \rangle}_{\text{production}} \quad (4.3)$$

The proper implementation of expression 4.3 can be verified by seeking to reproduce DSC (Differential Scanning Calorimetry) or ODTX (One-Dimensional Time to eXplosion) measured temperatures based

on kinetic mechanisms available in the literature.

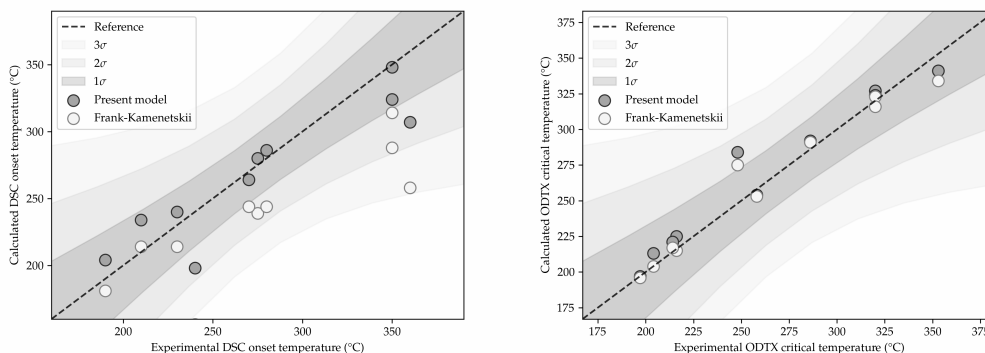


Figure 4.1. Experimental temperatures (x -axis) against calculated temperatures (y -axis) expressed in $^{\circ}\text{C}$. Dotted line illustrates the reference (perfect correlation). σ , 2σ and 3σ deviation are represented through shades of grey. Expression 4.3 (red) is compared to Frank-Kamenetskii theory (blue). Pearson correlation coefficients are 0.91 and 0.97 for DSC and ODTX, respectively. The left-hand graph describes decomposition “onset” temperatures (DSC) while the right-hand graph describes critical temperatures (ODTX).

Figure 4.1 shows the good agreement between calculated and experimental temperatures. However, it should be noted that this approach was simplified in some details. These include the consideration of the different phases (solid, liquid and gas), their interactions as well as the kinetics associated with the phase transitions, or even the defects allowing the vaporization of the decomposition gases leading to the formation of hot spots.

5 Preliminary theoretical pathways to sensitivities

In the previous sections, we have discussed local reaction mechanisms, the extraction of associated kinetic constants, the derivation of apparent kinetics from reaction paths and the thermal propagation of decomposition. Our starting point was in particular, on impact sensitivity. Specifically, the previous section showed that it was possible to describe the behaviour of an energetic material subjected to thermal stresses in a fairly simple way. Based on this principle, we now wish to verify that it is possible to trace back to dissipated mechanical stresses. The idea is to find sensitivity criteria, determined without empiricism for any model material considered. This approach, therefore, requires determining the relationship between the mechanical stress and the energy dissipated as heat [26]. For this purpose, the simplest assumption

was to consider an equivalence between the mechanical power supplied and the thermal power dissipated in the material.

Impact sensitivity The impact sensitivity test consists of dropping a mass M from a height h onto a 40mm^3 sample (during the test procedure). The pressure generated by the impact can then be simply estimated by $P = M g h / V$ (around 10^8 Pa). It can then be assumed that the propagation time of the shock wave is much shorter than that of the deformation and that it is therefore this wave that brings energy to the system. In a non-ideal case, the wave is absorbed as it propagates through the system. For simplicity, it can be assumed that a fraction η of the wave's entire energy is absorbed. Assuming that the mechanical power is equal to the thermal power, we then have an explicit relationship of 5.1 between h and the thermal heating.

$$\Delta T = \frac{\tau_{\text{dissipation}}}{\tau_{\text{impact}}} \cdot \frac{\eta (M g h / V)^2 V}{2m C_{p,m} \mathcal{E}_{\text{el}}} \quad (5.1)$$

Where $\sigma := M g h / V$ the peak pressure, η the dissipated mechanical energy fraction, V the system volume, \mathcal{E}_{el} the elastic modulus, m the system mass, $C_{p,m}$ the system-specific heat capacity, $\tau_{\text{dissipation}}$ the characteristic dissipation time and τ_{impact} the constraint duration. A quick numerical application with reasonable orders of magnitude yields $\Delta T \sim 10^6 \eta$. Therefore, it is reasonable to assume that only a small fraction of the shockwave is absorbed. By describing the wave absorption over time within the system, we can show that the fraction η evolves linearly with the system length L , leading more reasonably to $\Delta T = 10^2 \sim 10^3$.

Shock sensitivity The description of shock sensitivity is slightly less complex than impact. Indeed, a shock wave is generated and propagated through attenuation plates allowing for modulation of the incident wave's intensity on the sample. The "measured" shock sensitivity, therefore, corresponds to the length of this succession of plates: the greater the attenuation, the more sensitive the material, and vice versa. Using the expression 5.1, only a few simple changes are needed before reaching expression 5.2.

$$\Delta T = \frac{\tau_{\text{dissipation}}}{\tau_{\text{impact}}} \cdot \frac{\eta_{\text{dissipated}} (\eta_{\text{plates}} \sigma_{\text{peak}})^2 V}{2m C_{p,m} \mathcal{E}_{\text{el}}} \quad (5.2)$$

Shock sensitivity is then identified with attenuation η_{plates} or simply with pressure $\eta_{\text{plates}} \sigma_{\text{peak}}$.

Friction sensitivity In the friction sensitivity context, a force is applied to the sample modulating the contact interaction with a sliding plate with a velocity v . Experimental observation shows that in first approximation the intensity of kinetic friction only varies with the apparent weight of the object and the coefficient of kinetic friction, but not with the contact area or the velocity. However, the power associated with the work of friction explicitly shows the speed of friction as $P = \mathbf{F} \cdot \mathbf{v} = \mu N v$, where $\mu < 1$ is the friction coefficient. Expression 5.3 is then simply established.

$$\Delta T = \frac{\mu N v}{m C_{p,m}} \tau_{\text{dissipation}} \quad (5.3)$$

Note that the stress is initially applied to one of the sample surfaces and not to the complete sample itself.

6 Conclusion and outlook

Up to now, the theoretical characterization of the energetic materials' sensitivities remains an open problem overall. Despite the rather simple correlations proposed by the empirical literature in the field, the behaviour of energetic materials is extremely rich and complex. As illustrated above, it seems possible to overcome some of this complexity and satisfyingly describe their behaviour, without over-simplifying assumptions. It should be noted, however, that a physical description, even a simplified one, of the underlying phenomena remains much more expensive than any QSPR. Particularly, the search for reaction mechanisms and pathways leading to exothermic reactions seems to be a crucial procedure for a good description of the decomposition kinetics. However, recently developed tools and methods allow these problems to be tackled efficiently.

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