MODELING AND PREDICTION OF SENSITIVITY IN ENERGETIC MATERIALS

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Abstract. Sensitivity prediction is a complex problem. Many studies attempted to correlate experimental data with molecular and microscopic features. In the context of the well-recognized macroscopic hot spot model, an application of an original approach to predict impact sensitivity of 11 explosives is described in terms of parameters of explosive decomposition. This model provides a useful tool in the research for new explosives and the results do not depend on the calculation of solid-state formation enthalpy of explosives.

INTRODUCTION

Previously, some authors (1) have emphasized the difficulty in predicting mechanical sensitivity. This property may refer either to the ability to initiate chemical decomposition reactions, or to the capability of shock-to-detonation transition. Confusion may nevertheless occur. Even if in both aspects, molecular parameters linked to the chemical structure of the explosive play a role, other factors, at mesoscopic and microscopic levels, are not identically involved, under shock and under impact. Consequently, direct correlations between observed sensitivities and molecular structure (2) are to some extent arbitrary, despite satisfactory predictions, for instance, when the relationship depends on parameters not related to the well-known initiation mechanism, such as variables defined in terms of excited states of the isolated molecule (3).

Therefore, a preliminary compilation of the physical mechanisms that may enhance the initiation of the material is of paramount importance to identify relevant parameters. For instance, a model to investigate the magnitude of non-adiabatic effects (4) indicated that the fraction of excited molecules in the solid is lower than $10^{-4}$ for a typical insulator with a gap of 4 eV (5). As this upper bound decreases exponentially with the bandgap, electronic excitations are not expected to play any significant role for most energetic materials. With the additional assumption that the electrons remain in thermal equilibrium with nuclei in shock conditions, Kunz et al. obtained a corresponding excitation rate of $10^{15}$ (6). In this context, it appears reasonable to focus on the electronic ground state. In addition to a careful selection of model parameters on the basis of possible ignition mechanisms, further progress may be expected from experiments aimed at differentiating various contributions to sensitivity. For instance, in highly homogeneous materials, low sensitivities may be observed because of a lack of hot spots to propagate the chemical decomposition. To avoid such a dependence of the results on the concentration of defects, it is common to enhance hot spot formation with the help of abrasive paper. In the following, the results of such experiments are analyzed and applied using a simple model involving only three
parameters: density, explosion energy and volume increase associated with chemical decomposition.

EXPERIMENTAL ASPECTS

Drop-weight impact test experiments were carried out for 11 compounds (10 kg weight, 30 mg sample, 50 trials) using abrasive paper to enhance the number of hot spots. The experimental results are summarized in Figure 1.

FIGURE 1. Drop-weight impact sensitivity for studied explosives—h50(cm)

MODELS

In the model (7), impact sensitivity is defined by thermodynamical and kinetic characteristics of the thermal decomposition of the explosives. The higher the energy released in the decomposition products the greater the reactions, and the more sensitive the explosive. Sensitive explosives are also explosives with a low molecular packaging coefficient and a high void volume in the aggregate. In this case, the energy released is not dissipated in the lattice, but is available to break the molecular bonds.

The model provides a correlation between the structural parameter q', and log(h50):

\[ \log(h50) = L + Tq' \]  

(1)

L and T are deduced from the application of the regression equation to the previous experimental data; q' includes density, rate of decomposition (estimated from the molecular packaging coefficient and the volume of decomposition products) and energy released during explosion. This last factor requires the evaluation of solid-state formation enthalpy of explosives. The PIMM/SUB approach (8) is applied to predict this property. We use these values to calculate q', and the sensitivity and we compare the results with those obtained with the KARASH method in the original model.

In the PIMM/SUB approach, solid-state formation enthalpies are evaluated as the difference between gas-phase values \( \Delta H_f(gas) \) and sublimation enthalpies \( \Delta H_{sub} \). \( \Delta H_f(gas) \) is estimated from the PIMM force field and explicit expressions are used to represent the short Van der Waals interactions at the molecular surfaces, the electrostatic energy and the hydrogen bond contribution in the calculation of \( \Delta H_{sub} \).

RESULTS AND DISCUSSION

In Figure 2, we compare solid-state formation enthalpies calculated with the KARASH and the PIMM models. These results are applied to estimate and to compare q' according to the model for formation enthalpies calculations. Results are given in Figure 3.

FIGURE 2. Solid-state formation enthalpy (kcal/mol)
Experimental results, as shown in Figure 1, lead us to divide explosives into two categories. On one side, TATB, NTO, DANTNP and ANTA, the less sensitive ones, and on the other side, the explosives with a lower drop-weight impact sensitivity (h50). The complexity of sensitivity prediction when a new explosive is designed doesn’t permit ranking within the categories of high sensitivity or low sensitivity but the determination of low sensitivity is useful for synthesis purposes.

As expected, results in Figures 1 and 3 show that, as a whole, the less sensitive explosives give the lowest molecular parameter $q'_{v}$. Only TNT and DINGU are more sensitive in the drop-weight impact test than predicted by the model. Moreover, despite discrepancies, for HMX, DNAT and HNAB, between the predicted solid-state formation enthalpies, either with the KARASH model, or the PIMM/SUB model, these explosives are always predicted sensitive, in accordance with experimental data. So, predicted sensitivities do not depend to a great extent on the method used to calculate formation enthalpies.

CONCLUSION

An original model was developed in the macroscopic frame of the phenomenology of hot spots to predict impact sensitivity of explosives. To overcome the difficulty of hot spot formation, drop-weight impact experiments with abrasive paper were performed. A correlation between experimental data and molecular features was proposed after an analysis of the processes involved in impact initiation, at molecular, mesoscopic and macroscopic scales. Despite the complexity of the problem, this model is a useful tool to guide the molecular design of new explosives.

It requires calculation of parameters and we showed that uncertainty in one of them, the solid-state formation enthalpy of explosives, is not harmful to results. More experimental data on explosives with various chemical structures are required. This collection of data with well-defined and well-known conditions is of prime importance. Confirmation of another hypothesis, incompleteness of combustion during explosion, is also expected.

Our future goal is to propose an improvement of the predictive approach to sensitivity by focusing on kinetic aspects of decomposition, for instance, by introducing an activation energy parameter in the correlation.

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REFERENCES

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