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# Towards improved models to rationalize and estimate the decomposition temperatures of nitroalkanes, nitramines and nitric esters[☆]

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## Abstract

Decomposition temperatures have been compiled for a set of 24 compounds including nitroalkanes, nitramines and nitric esters. In an attempt to rationalize their values, correlations involving either the dissociation energy for the weakest bond in the molecule or the proportion of trigger linkages are investigated. The latter quantity correlates fairly well with thermal stabilities. A simple model based on kinetic parameters associated with the breaking of trigger linkages allows the estimation of decomposition temperatures with an average absolute deviation from experiment $<11\,^\circ\mathrm{C}$ and no error $>30\,^\circ\mathrm{C}$, except two outliers with errors $\simeq 70$–$80\,^\circ\mathrm{C}$. The latter are associated with nitramines bearing esters or furazan moieties, which prove less stable than expected on the basis of their number of trigger linkages.
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## 1. Introduction

Nitro compounds are used in various fields, ranging from pharmacology to energetic materials. For some years, the design of such compounds has been made more efficient through the use of modeling approaches, such as quantitative structure-activity relationships (for drugs) or the a priori calculation of the density and energy content (for explosives and propellants). However, whatever the application, evaluation of the stability of new molecules is of paramount interest. Most applications require a fair stability and avoiding attempts to synthesize unstable compounds should contribute to a reduction of risks. In this context, estimation of decomposition temperatures should be carried out before the actual synthesis of a compound.

The main approach presently available for this purpose relies on group contributions. As it requires a very extensive parameterization, it is especially developed for polymers for which a large body of experimental data is available on

materials made from similar building blocks. The details of the method have been reported by van Krevelen [1]. Later, a topological method was introduced by Bicerano to extend the scope of the group contribution scheme of van Krevelen, but this approach is also restricted to polymers [2]. Bond dissociation energies (BDEs) are commonly used as a criterion to assess the stability of new compounds [3,4]. This is a natural approach as thermal decomposition consists of breaking chemical bonds, which gets easier as the thermal energy per atom gets closer to the smallest BDEs. Moreover, for nitro compounds, it is usually assumed that the $\mathrm{X}$–$\mathrm{NO_2}$ bonds play the role of trigger linkages for the decomposition process [5]. Thus, some studies focus on the BDE of the weakest bond of the molecule under consideration, hereafter denoted $\mathrm{BDE}_W$. For instance, a correlation between the impact sensitivity of nitroaromatics and $\mathrm{BDE}_W$ was recently reported [4]. Nonetheless, BDEs might not be a very reliable measure of the strength of the trigger linkages, as they are typically derived from theoretical calculations in gas phase. On the other hand, whenever several bonds in the molecule are similarly weak, it is clear that all of them should be taken into account. In fact, improved models for the decomposition temperature ($T_{\mathrm{dec}}$) should combine the advantages of the group contribution method which takes into account the trigger linkages

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concentration $n_W$, and of the BDE based approach which considers the strength of individual bonds.

As a first step along such lines, a set of nitro compounds, including nitroalkanes, nitramines and nitric esters is considered. First, the relationships between $T_{dec}$ and $BDE_W$ on one hand, and between $T_{dec}$ and $n_W$ on the other hand, are investigated. Then, a theoretical definition of the decomposition temperature that does not depend on the details of the measurement technique is put forward, providing a simple analytic relation for $T_{dec}$ involving both $BDE_W$ and $n_W$. Finally, some decomposition temperatures are estimated from the present model.

## 2. Correlations involving decomposition temperatures

For the present study, experimental $T_{dec}$ data have been compiled for some nitrocompounds, using either values recorded in the ICT database [6] or measured in the analytical laboratory at CEA-Le Ripault with differential scanning calorimetry. Unfortunately, the details of the measurements were not systematically attached to the value recorded. However, it is interesting to investigate to what extent simple assumptions are consistent with the $T_{dec}$ values in primary sources. Obviously, for further developments of semi-quantitative models, a more careful selection of reference data is desirable. The present study is restricted to materials which decompose in the melt, i.e. whose melting point is lower than their decomposition temperature. This excludes some well-known energetic materials such as HMX for which a percolation model has been put forward for the solid-state decomposition [7]. Nitroaromatics were not considered either due to their complex decomposition mechanisms.

The compounds studied fall into three sets: nitroalkanes with $C–NO_2$ bonds (Fig. 1), nitramines with $N–NO_2$ bonds (Fig. 2) and nitric esters with $O–NO_2$ bonds (Fig. 3). The BDE of every $X–NO_2$ bond was computed as the difference between B3LYP/6-31G* energies calculated for HF/3-21G* equilibrium structures, corresponding either to the molecule under investigation or to the fragments obtained after cleav-

Table 1
Weak bond dissociation energies $BDE_W$ (kJ/mol), ratio of the number of weak bonds (trigger linkages) to the total number of chemical bonds $n_W$ (%), calculated ($T_{dec}^{calc}$) and observed ($T_{dec}^{obs}$) decomposition temperatures (in °C) for some nitro compounds

| Compound | $BDE_W$ | $n_W$ | $T_{dec}^{calc}$ | $T_{dec}^{obs}$ |
|---|---|---|---|---|
| (1) | 145 | 16.2 | 213 | 202 |
| (2) | 109 | 19.3 | 200 | 205 |
| (3) | 165 | 12.5 | 235 | 232 |
| (4) | 269 | 10.0 | 255 | 246 |
| (5) | 161 | 11.7 | 240 | 260 |
| (6) | 166 | 14.3 | 222 | 211 |
| (7) | 176 | 8.1 | 295 | 227 |
| (8) | 115 | 6.7 | 325 | 246 |
| (9) | 168 | 11.8 | 244 | 246 |
| (10) | 192 | 8.3 | 291 | 307 |
| (11) | 242 | 5.3 | 367 | 360 |
| (12) | 152 | 15.0 | 159 | 152 |
| (13) | 177 | 11.5 | 198 | 182 |
| (14) | 162 | 13.8 | 171 | 185 |
| (15) | 181 | 9.1 | 238 | 242 |
| (16) | – | 12.5 | 185 | 190 |
| (17) | – | 24.1 | 182 | 176 |
| (18) | – | 18.5 | 202 | 181 |
| (19) | – | 20.0 | 195 | 186 |
| (20) | – | 14.3 | 223 | 192 |
| (21) | – | 13.3 | 204 | 201 |
| (22) | – | 13.0 | 198 | 202 |
| (23) | – | 13.6 | 210 | 205 |
| (24) | – | 12.1 | 217 | 219 |

age of the bond. In the latter case, two calculations were carried out separately on the $X^\bullet$ and $XNO_2^{\bullet\bullet}$ radical fragments, using the unrestricted Hartree–Fock and Kohn–Sham formalisms, respectively, for the optimizations and single-point calculations. All quantum chemical calculations were carried out with the Jaguar program [8]. Zero-point and thermal energies were neglected.

The results are reported in Table 1, together with the reported decomposition temperatures $T_{dec}^{obs}$. As illustrated by the plot of $T_{dec}$ versus $BDE_W$ shown on Fig. 4, materials with weaker bonds tend to be more thermally unstable. This is especially clear for the nitramine family of compounds. However, Fig. 5 shows that $T_{dec}$ correlates even better with $n_W$. In this Figure, the polynitro family refers to compounds
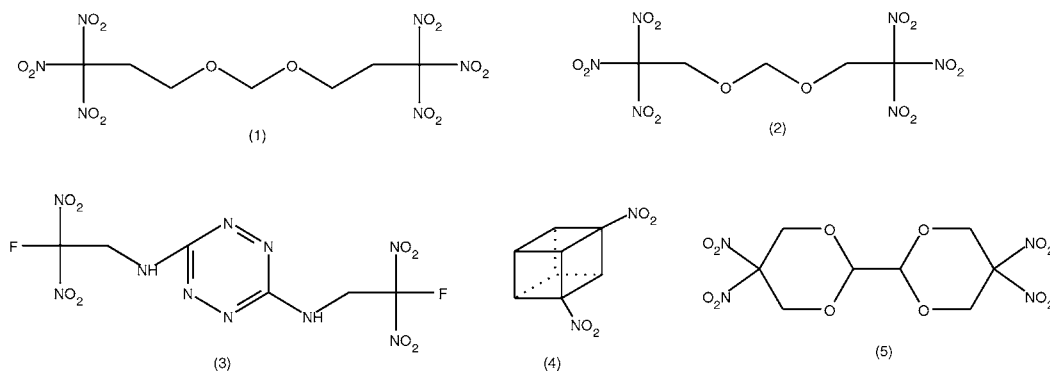


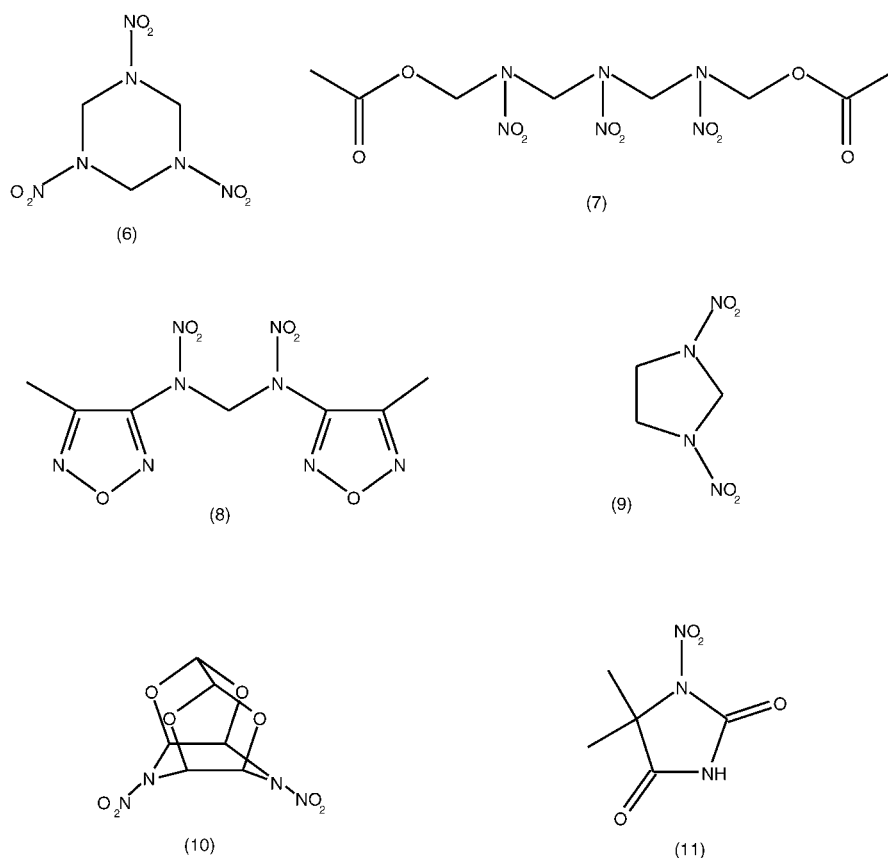Fig. 1. Nitroalkanes studied in present work.
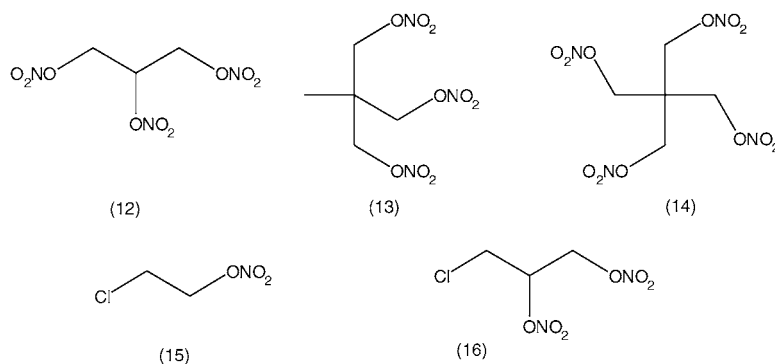
Fig. 2. Nitramines studied in present work.

Fig. 3. Nitric esters studied in present work.

with several kinds of X–NO$_2$ bonds, shown in Fig. 6. The good correlation between $T_{dec}$ and $n_W$ indicates that the number of trigger linkages provides a more reliable assessment of thermal stabilities than theoretical bond strengths for these compounds. This supports the use of group contribution techniques. Indeed, it may be anticipated from Fig. 5 that group contributions associated with X–NO$_2$ bonds should provide fair estimates of $T_{dec}$, especially if different parameters are introduced according to the identity of the X atom. In the remainder of this paper, no attempt is made to account for the theoretical BDEs reported in Table 1. The influence of

the latter is only implicitly included through suitable kinetic parameters for each kind of bond. Thus, the different bond strengths within a same class of X–NO$_2$ bonds are completely neglected. In practice, this approximation avoids the need for time-consuming quantum chemical calculations.

## 3. Kinetic model of bond breaking

The results of the preceding section suggest that every weak bond on a molecule should be considered as a potential
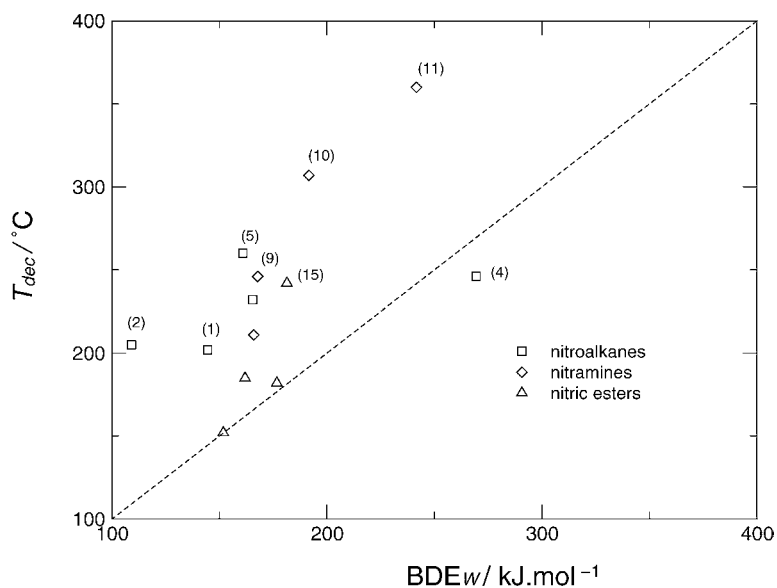
Fig. 4. Plot of experimental decomposition temperatures vs. the lowest bond dissociation energy calculated at the B3LYP/6-31G* level of theory for some of the compounds studied.

trigger linkage. The question arises as to the respective weight of different bonds. To precise this point, it is useful to start from kinetic considerations. Since there is presently no means to know precisely the decomposition path for molecules in heated materials, activation energies cannot be defined rigorously on the basis of equilibrium and transition states structures, nor is it possible to assess the time dependence of the concentrations of intermediary species. In this context, we focus on the starting point, i.e. on the intact material before decomposition begins, and especially on chemical bonds. For every distinct kind $W$ of trigger linkage, $N_W$ denotes the number of trigger bonds of type $W$ in the sample considered. As the sample is maintained at temperature $T$, we denote by $N(t)$

the total number of chemical bonds not yet damaged by the decomposition process at time $t$, starting with no broken bond at $t = 0$. In addition, it is assumed that the reaction rate is controlled by the rupture of the trigger linkages. Diffusion may reasonably be neglected as a limiting factor since only decompositions occuring in the melt are considered here. Thus, the following equation is obtained for the reduced reaction rate $k$:

$$k = -\frac{1}{N}\frac{dN}{dt} = \frac{1}{N}\sum_W N_W A_W e^{-E_W/kT} \tag{1}$$

where the sum is over the various kinds $W$ of trigger linkage. The kinetic parameters for bonds of type $W$ are $A_W$
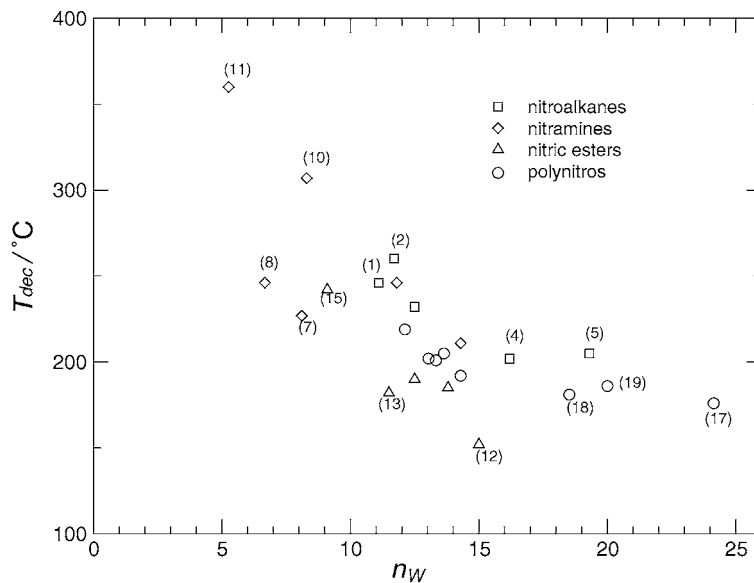


Fig. 5. Plot of experimental decomposition temperatures vs. the trigger linkage concentration $n_W$ for the compounds studied.
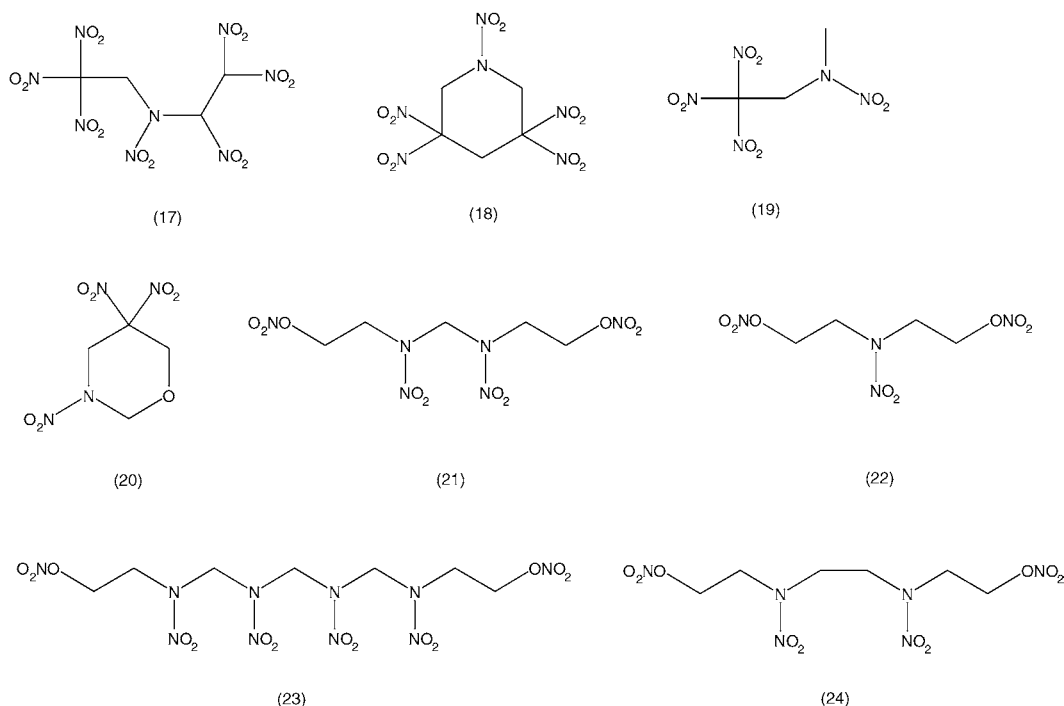
Fig. 6. Compounds not used for model parameterization, referred to as polynitros in this work as each has various kinds of X–NO$_2$ bonds.

(pre-exponential factor) and $E_W$ (activation energy for bond dissociation). Eq. (1) is clearly oversimplified. For instance, it does not include the autocatalytic character of the decomposition. As a result, it cannot account for any increase of $k$ during the decomposition process. Nevertheless, it is consistent with the trigger linkage model which suggests that $T_{\text{dec}}$ might be estimated from the critical initiation step only.

Whatever the equation used for the time evolution of $N$, a proper definition of $T_{\text{dec}}$ at the microscopic level is needed. The decomposition temperature might be defined according to the time it takes for 50% of the bonds in the sample to be damaged, or according to the proportion of damaged bonds after a given delay. However, such definitions involve arbitrary parameters. Thus, in this work, $T_{\text{dec}}$ is defined as the temperature for which the maximum value of $k$ over time equals a critical constant $k_c$, the same for all the compounds considered. Using Eq. (1) for the time evolution of $N$, this maximum value corresponds to $t = 0$ since $k$ cannot increase. Hence $T_{\text{dec}}$ may be obtained as a solution of Eq. (2) :

$$\sum_W \left( \frac{N_W}{N} \right) A_W e^{-E_W / kT_{\text{dec}}} = k_c \qquad (2)$$

To turn this equation into a practical model, the various bond types, i.e. bonds with the same kinetic parameters, have to be defined. In this work, a single pair of values $(A_W, E_W)$ is assumed for each of the three classes of bonds studied, namely C–NO$_2$, N–NO$_2$ and O–NO$_2$. In fact, it is clear from Eq. (2) that the absolute values of $A_W$ and $k_c$ are irrelevant. Indeed, only the dimensionless ratio $a_W = A_W / k_c$ really matters. It is interesting to note that for the compounds with a single type

$W$ of trigger linkage, Eq. (2) may be solved analytically:

$$\frac{1}{kT_{\text{dec}}} = \frac{1}{E_W} \ln \left( a_W \frac{N_W}{N} \right) \qquad (3)$$

The same equation may be obtained whenever one bond has a significantly lower activation energy $E_W$ than all others, because in that case its contribution is predominant in the right hand side of Eq. (1). Eq. (3) suggests that $T_{\text{dec}}$ should exhibit a simple (quasi-linear) dependence on $E_W$ for compounds with similar concentrations of trigger linkages. Furthermore, assuming that the activation energy essentially depends on the associated BDE for a given kind of bond, the correlation illustrated in Fig. 4 between $T_{\text{dec}}^{\text{obs}}$ and BDE$_W$ is understandable. The next section focusses on the role of the ratio $n_W = N_W / N$ of trigger linkages to the total number of bonds in the sample. Since only pure materials are considered, the proportion of trigger bonds with respect to the total number of chemical bonds may be estimated considering only one molecule.

## 4. Calculation of decomposition temperatures

To apply the previous analytic expression for $T_{\text{dec}}$, the compounds showing C–NO$_2$, N–NO$_2$ and O–NO$_2$ are considered separately. Within each of the three sets, all trigger bonds are assumed to share only two kinetic parameters ($a_W$, $E_W$). Then, the calculation of $T_{\text{dec}}$ requires only $n_W$ as input. The kinetic parameters are adjusted so as to reproduce the observed decomposition temperatures of the compounds in each
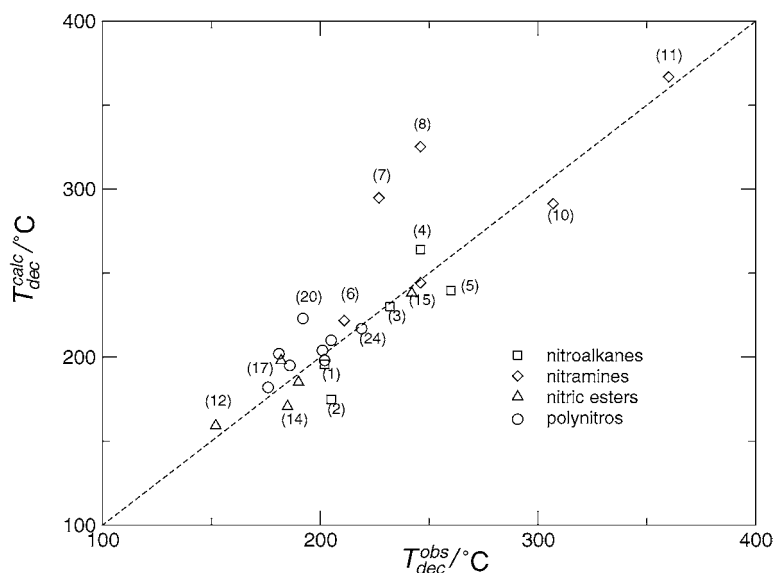
Fig. 7. Plot of calculated vs. experimental decomposition temperatures for the compounds studied

set. The values obtained are reported in Table 2. It may be noted that the three activation energies thus obtained are consistent with the relative stabilities of nitroalkanes, nitramines and nitric esters. Then, the present model is applied to calculate $T_{dec}$ values for the compounds in the calibration set and for additional compounds (Fig. 6) not used in the parameterization. Because the latter exhibit different X–NO$_2$ bond types, Eq. 2 was solved numerically for $T_{dec}$. For all 24 compounds studied, calculated decomposition temperatures are plotted against experimental ones in Fig. 7. The results prove encouraging, notwithstanding two outliers, compounds (7) and (8) whose $T_{dec}$ are overestimated by $\simeq$ 70–80 °C. In fact, since these two compounds do not fit well in the present model, they were excluded from the parameterization of the nitramine moiety. They are the only nitramines that have ester and furazan groups, which could contribute to initiate the decomposition process. The low stability of compound (8) is readily explained as this molecule exhibits especially weak trigger bonds, with BDE$_W$ = 115 kJ/mol (values of BDE$_W$ for the other nitramines are all larger than 165 kJ/mol). For compound (7), although the presence of ester moieties might play a role in the decomposition process, the latter probably do not make the initiation easier, as the stability of this molecule is similar to that of RDX (compound (6)). The central part of the molecule, made from nitramine groups associated with methylene CH$_2$ units, is equilibrated with regard to its oxy-

gen balance. Therefore, it may decompose into stable gaseous products (H$_2$O, N$_2$, CO), thus providing a significant energy, whatever the other chemical moieties present in the material. In this context, the decomposition temperature of such a compound might be determined by the oxygen-equilibrated part, rather than by the trigger linkages distribution.

All in all, the average absolute error of predicted decomposition temperatures is only 16 or 11 °C if the two outliers are disregarded. In the latter case, all errors lie within 30 °C of experiment. The good results (average error = 10 °C) obtained for polynitro compounds, which were not used for deriving the kinetic parameters, is especially encouraging.

## 5. Conclusion

In future work, further investigations of the reliability and limitations of the present approach, considering more extensive datasets, are desirable. It would be specially interesting to apply this scheme to strained compounds, for which alternative reaction paths can be made possible provided they are associated with strain releases. For instance, it has been suggested that the primary step of the decomposition of nitrocubanes involves scission of C–C (rather than C–NO$_2$) bonds [9]. Therefore, the good fit obtained for dinitrocubane (compound (4) on Fig. 1) might be somewhat misleading, since the model assumes a decomposition triggered by the scission of the C–NO$_2$ bonds. On the other hand, the assumption that the value for $T_{dec}$ depends only on the rate of decomposition in the early stages (i.e. when the number of damaged bonds is very small with respect to the total number of chemical bonds) remains to be validated.

On the other hand, a method to estimate decomposition temperatures for nitroaromatics would be even more use-

Table 2
Reduced preexponential factors $a_W$ and activation energies $E_W$ (K) for the three kinds of trigger linkages considered here

| Bond type | $a_W$ | $E_W$ |
|---|---|---|
| C–NO$_2$ | 2840 | 2985 |
| N–NO$_2$ | 576 | 2183 |
| O–NO$_2$ | 171 | 1402 |

ful. Preliminary investigations reveal the following: (a) as it stands, the present model cannot handle nitroaromatic compounds (b) bond dissociations energies seem to have a more significant role than found for the compounds investigated in this work.

Assessing the relative influence of the number and strength of trigger linkages on stability, the present work opens perspectives for decomposition temperature models taking fully into account the distribution of bond strengths in the molecule. To take advantage of the fairly accurate bond strengths that may be obtained from quantum chemical calculations, the latter should be related to the condensed phase activation energies $E_W$ involved in the present kinetic model. For instance, the relatively small BDE of the nitramine compound (8) should be reflected by a specially small value of the activation energy $E_W$.

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