A new method to predict activation energies of nitroparaffins

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A novel relationship has been derived to predict the activation energies ($E_a$) of low-temperature non-autocatalyzed thermolysis of nitroparaffins through suitable combination of elemental composition. The new correlation of $E_a$ is based on the experimental data using the isothermal monomeric method, which is useful method to examine the kinetics of thermolysis of energetic materials in vacuum. The new method uses the optimized number of carbon, hydrogen and oxygen divided by molecular weight of nitroparaffins to obtain a reliable correlation. The new correlation is a general relationship because it can be applied for various nitroparaffins as compared to previous method which uses oxygen balance for some specific groups of mentioned compounds. $R$-squared value or the coefficient of determination of the new correlation is 0.954.

Performance, thermal properties and sensitivity are the most important parameters in searching of new energetic materials. The possibility of predicting mentioned parameters would provide significant cost savings, increase the safety of storage and testing of these compounds and provide for greater control of the performance of these energetic materials. Various empirical methods complemented the computer output for desk calculations of factors related to some important aspects of energetic compounds are important to chemist and the chemical industry\textsuperscript{1,2}. It should be emphasized that initiating mechanism of detonation has always been responsible for frequent injuries and crashes. However, safety engineering requires that important parameters for initiating energetic materials should be understood\textsuperscript{3}.

It is necessary to have explosives with sufficient stability from the standpoint of their functional properties, safety in handling and long-term storage capacity. The knowledge of the thermal stability of energetic compounds is the most significant from the point of view of technological practice. The most widely used methods to examine the kinetics of thermolysis of energetic materials in vacuum is the isothermal manometric method with a glass compensating manometer of the Bourdon type, which was named as Soviet Manometric Method (SMM)\textsuperscript{3}. The SMM is the isothermal manometric method in the Russian version that can be used for the kinetics determination of the non-autocatalysed initial stage of explosives thermolysis. Due to the effects of consecutive reactions of intermediates and products of thermal decomposition both with each other and with the starting energetic material, the most sophisticated method is SMM method which can remove gaseous intermediates from the sample measured\textsuperscript{4}. Physical and chemical stability of explosives can also be specified using thermoanalytical methods such as differential thermal analysis (DTA), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) methods\textsuperscript{5}. However, the results of some methods of the DSC are directly comparable with the results of SMM\textsuperscript{5,6}. Moreover, if a relationship such as a calibration curve exists between results of the DTA and TGA with the results of the SMM, the results of DTA and TGA can be converted to SMM data\textsuperscript{7-9}.

Thermal stability of nitroparaffins and their derivatives was studied through the influenced exercised by molecular structure\textsuperscript{5}. Zeman and coworkers\textsuperscript{10,11} have studied on different classes of polynitro compounds to attribute the Arrhenius parameters of low temperature decomposition to some specific parameters of different compounds such as the $^{15}$N NMR chemical shifts and the electronic charges at nitrogen atoms of the nitramines. Zeman\textsuperscript{12-14} has also derived a linear relationship between oxygen balances of polynitroparaffins to activation energy of thermolysis of these compounds, which has satisfied for selected groups of

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nitroparaffins. The purpose of this work is to present a new simple general scheme for obtaining activation energy of polynitroparaffins through optimized elemental composition. It will be shown that optimized elemental composition can provide more reliable prediction as compared to oxygen balance for polynitroparaffins. Since data on the thermal reactivity of polynitroparaffins in the condensed state are rare in literature, predicted results correspond almost exclusively to thermolysis in the gaseous state.

Using optimized elemental composition

Kamlet and Adolph\textsuperscript{15,16} used a method for estimating impact sensitivity based on the molecular structure of polynitroaliphatic compounds as well as nitroaromatics, nitroaromatics with a ring methyl group and nitrarnines. Kamlet\textsuperscript{15} defined oxygen balance for these nitrocompounds with a general \( \text{C}_a\text{H}_b\text{N}_c\text{O}_d \) formula as:

\[
\text{OB}_{100} = \frac{100(2d - b - 2a - 2n_{\text{COO}})}{\text{Molecular weight}} \quad \ldots (1)
\]

where \( \text{OB}_{100} \) is the oxygen balance of the given polynitrocompound \( n_{\text{COO}} \) is the number of carboxylate in the molecule. The relationship between impact sensitivity and oxygen balance for polynitroaliphatic compound has the following form:

\[
\log H_{50} = 1.74 - 0.23\text{OB}_{100} \quad \ldots (2)
\]

where \( H_{50} \) is the height at which 50\% of fall-hammer (weight 2.5 kg) tests were positive. Zeman and coworkers\textsuperscript{12-14} introduced a similar relationship for nitramines, nitrosoamines and nitroesters as well as nitroparaffins of the general form:

\[
\ln E_a = a_i + b_i\text{OB}_{100} \quad \ldots (3)
\]

where \( a_i \) and \( b_i \) are regression coefficients for different subgroups of mentioned classes of energetic compounds; \( E_a \) is the activation energy of low-temperature non-autocatalyzed thermolysis. Since Eq. (3) can be applied only for selected subgroups of different classes of nitrocompounds, there is some limitations for their applications as general correlations.

It was recently found that suitable combinations of elemental composition and some structural parameters for different classes of \( \text{C}_a\text{H}_b\text{N}_c\text{O}_d \) give more reliable impact sensitivity predictions as compared to Kamlet method\textsuperscript{15,16}. Moreover, the new correlations can provide simple reliable predictions as compared to outputs of complicated quantum mechanical methods\textsuperscript{17-21}. One can use a new scheme to derive useful equation for predicting activation energy of nitroparaffins on the basis of suitable combination of elemental composition. As

<table>
<thead>
<tr>
<th>Chemical name</th>
<th>Molecular structure</th>
<th>((E_a)_{\text{exp}})</th>
<th>((E_a)_{\text{cal}})</th>
<th>Dev</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitromethane</td>
<td>(\text{CH}_2\text{NO} )</td>
<td>227.19</td>
<td>238.64</td>
<td>-11.45</td>
</tr>
<tr>
<td>Trinitromethane</td>
<td>(\text{CH(ONO}_2 \text{)}_3)</td>
<td>177.4</td>
<td>169.06</td>
<td>8.34</td>
</tr>
<tr>
<td>Tetranitromethane</td>
<td>(\text{C(ONO}_2 \text{)}_3)</td>
<td>159.83</td>
<td>160.23</td>
<td>-0.40</td>
</tr>
<tr>
<td>Nitroethane</td>
<td>(\text{CH}_2\text{CH}_2\text{NO} )</td>
<td>253.55</td>
<td>242.21</td>
<td>11.34</td>
</tr>
<tr>
<td>1,1-Dinitroethane</td>
<td>(\text{CH}_2\text{CH(ONO}_2 \text{)}_2)</td>
<td>197.15</td>
<td>193.91</td>
<td>3.24</td>
</tr>
<tr>
<td>1,1,1-Trinitroethane</td>
<td>(\text{CH}_2\text{C(ONO}_2 \text{)}_3)</td>
<td>180.75</td>
<td>175.26</td>
<td>5.49</td>
</tr>
<tr>
<td>Hexanitroethane</td>
<td>(\text{C(ONO}_2 \text{)}_2\text{C(ONO}_2 \text{)}_3)</td>
<td>149.79</td>
<td>155.24</td>
<td>-5.45</td>
</tr>
<tr>
<td>1,1-Dinitropropane</td>
<td>(\text{CH}_2\text{CH}_2\text{CH(ONO}_2 \text{)}_2)</td>
<td>200.83</td>
<td>199.81</td>
<td>1.02</td>
</tr>
<tr>
<td>2,2-Dinitropropane</td>
<td>(\text{CH}_2\text{C(ONO}_2 \text{)}_2\text{CH}_2)</td>
<td>198.74</td>
<td>199.81</td>
<td>-1.07</td>
</tr>
<tr>
<td>1,1,1-Trinitropropane</td>
<td>(\text{CH}_2\text{CH}_2\text{C(ONO}_2 \text{)}_3)</td>
<td>176.98</td>
<td>180.66</td>
<td>-3.68</td>
</tr>
<tr>
<td>1,1-Dinitrobutane</td>
<td>(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH(ONO}_2 \text{)}_2)</td>
<td>201.5</td>
<td>204.73</td>
<td>-3.23</td>
</tr>
<tr>
<td>1,1,1-Trinitrobutane</td>
<td>(\text{CH}_2\text{CH}_2\text{C}_2\text{CH(ONO}_2 \text{)}_3)</td>
<td>182.42</td>
<td>185.41</td>
<td>-2.99</td>
</tr>
</tbody>
</table>

rms deviation (kJ/mol) 6.02

Table 1—Comparison of predicted activation energies (kJ/mol) of nitroparaffins in the gaseous state with the experimental data\textsuperscript{22-24} on the basis of SMM method.
KESHAVARZ: ACTIVATION ENERGIES OF NITROPARAFFINS

mentioned before, experimental data using SMM corresponding to thermolysis in the gaseous state were used in this work. The suitable correlation can be given as follows:

\[ \ln E_a = x_1 + x_2 \text{SCEC} \quad \ldots (4) \]

where SCEC is the suitable combination of elemental composition, which can be determined by regression of the measured values. Experimental data given in Table 1 were used to find SCEC which can be defined by the relation:

\[ \text{SCEC} = 0.3517a' + 0.1505b' + d' \quad \ldots (5) \]

where \( a' \), \( b' \) and \( d' \) are the number of carbons, hydrogens and oxygens divided by molecular weight of nitroparaffins. As seen in Eq. (5), the contribution of the number of nitrogen atoms is not important. According to Eq. (4), linear correlation can be expressed as follows:

\[ \ln E_a = 1.1914 \text{SCEC} \quad \ldots (6) \]

Figure 1 shows the experimental data of activation energies of nitroparaffins in the gaseous state as a function of suitable combination of elemental composition. \( R \)-squared value or the coefficient of determination of the new correlation is 0.954. Table 1 presents a set of the studied polynitroparaffins and experimental values of activation energies, \( E_a \), of their low-temperature thermolysis under conditions of the SSM, taken from Russian papers 22-24. Comparison of predicted results with the measured values is also given in Table 1. As seen in Table 1, activation energies predicted using Eq. (5) have a root mean square of deviation of 6.02 kJ/mol from the measured values. However, the results are in good agreement with values obtained from the measured data. As indicated in Table 1, the estimated activation energies of nitroparaffins by new correlation are within ±6.0 kJ/mol of the average of reported values for 9 compounds and more than ±6.0 kJ/mol for remainder 3 energetic compounds.

**Conclusions**

The new method provides a novel simple procedure for predicting activation energies of nitroparaffins. This work has introduced a new correlation so that it uses elemental composition in form SCEC rather than OB100. Eq. (6) will be valuable in directing research efforts towards design of nitroparaffins with desired activation energy in the gaseous state. Only elemental composition without using any experimental data or computed values would be needed to calculate activation energy in this new method. Predicted results on the basis of SMM method in Table 1 are compared with experimental data which may be taken as appropriate validation of the new procedure.

**Acknowledgement**

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**References**


Fig. 1—Activation energies of nitroparaffins in the gaseous state as a function of suitable combination of elemental composition.