

Two Dominant Factors Influencing the Impact Sensitivities of Nitrobenzenes and Saturated Nitro Compounds

Chenzhong Cao^{*,†} and Shuo Gao^{†,‡}

School of Chemistry and Chemical Engineering, Hunan University of Science and Technology, Xiangtan, 411201, People's Republic of China, and School of Chemistry and Chemical Engineering, Central South University, Changsha, 410083, People's Republic of China

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The factors governing the impact sensitivity (H_{50}) of nitrobenzenes and saturated nitro compounds were studied. It was observed that the oxygen balances (OB_{100}) and nitro group charge (Q_{NO_2}) are two important factors influencing the stability of these nitro compounds. Employing the square of nitro group charge ($Q_{NO_2}^2$) and OB_{100} as the parameters, a good quantitative model was built for predicting H_{50} of the above two sorts of nitro compounds. The predictive ability of the model was assessed by the cross-validation method (i.e., leave-one-out cross-validation). The cross-validation result shows that the model is significant and stable, and the predicted accuracy is within 0.21 m. This quantitative model may be a useful tool for the design of high-energy-density materials.

1. Introduction

Nitro compounds are a type of high-energy-density material (HEDM), and they are widely used for explosives. Today, they are still the main and most important explosives for civil as well as military applications. For HEDMs, the higher performance, of course, has always been a prime requirement in the field of research and development of explosives. However, the safety, reliability, and stability of HEDMs also need to be taken into account. The impact sensitivity, usually expressed as the impact sensitivity index (i.e., H_{50}), is one of the qualities to scale the reliable performance of energetic materials, and it is usually measured by drop-weight impact tests. The impact sensitivity is the key enabling nitro compounds to possibly be used in security. However, the experimental measurement of the H_{50} value is time-consuming and sometimes unreliable.¹ Meanwhile, it is impossible to measure the H_{50} value for yet unsynthesized energetic materials. Consequently, establishing the quantitative relationship between the sensitivity and molecular structure of nitro compounds by theoretical approaches has become an urgent and important subject, which has been given considerable attention in the last decades, and some criteria were proposed to aid the evaluation of an explosive hazard.

It was considered that the fission of C–NO₂, N–NO₂, and O–NO₂ bonds is the trigger step in nitro explosives. Therefore, Delpuech and Cherville^{2–4} investigated the relationships between the thermal sensitivities and the properties of the C–NO₂, N–NO₂, and O–NO₂ bonds in nitro compounds. Owens,⁵ Xiao,⁶ and Song⁷ studied the relationship between the impact sensitivity and the weakest C–NO₂ bond dissociation energy of nitro compounds, respectively. The electrostatic potential on the molecular surface⁸ and ¹³C and ¹⁵N NMR chemical shifts⁹ were also used to relate to the sensitivity of nitro compounds. Kamlet and Adolph¹⁰ even employed the oxygen balances

(OB_{100} , calculated by eq 1) to estimate the impact sensitivities of some nitro compounds:

$$OB_{100} = \frac{100(2n_O - n_H - 2n_C - 2n_{COO})}{M} \quad (1)$$

where n_O , n_H , and n_C represent the numbers of O, H, and C atoms in the molecule, n_{COO} is the number of carboxyl groups, and M is the molecular weight. Correlations between the impact sensitivities and oxygen balances reported by Kamlet and Adolph¹⁰ have been widely applied in the field of energetic materials research. It should be noted that OB_{100} reflects only the information about the chemical composition of a compound and does not reflect that about molecular structure. Perhaps, OB_{100} is one of the main factors affecting the sensitivity of nitro compounds.

It was interesting that Bates¹¹ used the electron-attraction ability of the substituents to relate the sensitivity of tetrazole. Zhang¹² recently developed this idea to investigate the correlation between impact sensitivities and nitro group charges in nitro compounds. However, there is still room for improvement in the above-mentioned works, namely, “these criteria and correlation methods are valid only for the special cases or usually have certain limits” and “there is not a monotonic relationship between impact sensitivities and nitro group charges”.¹² In addition, the following questions are still not answered: How does one quantify the impact sensitivity of a nitro compound from its molecular structure, and how many main factors affect its impact sensitivity? Having made many investigations, we find that the impact sensitivities of nitrobenzenes and saturated nitro compounds can be quantified by two factors: nitro group charge and oxygen balances.

The present study perhaps provides new insight into understanding the effects of the molecular structure on the impact sensitivities for nitro compounds, and may be instructive to the security and design of HEDMs of nitro compounds containing the elements C, H, N, and O.

* Corresponding author. Tel.: +86 0732 8291336; fax: +86 0732 8290509; e-mail address: czcao@hnust.cn.

[†] Hunan University of Science and Technology.

[‡] Central South University.

TABLE 1: The Experimental Impact Sensitivities and Structural Parameters for Some Nitrobenzenes and Saturated Nitro Compounds

| compound ^a | Q_{NO_2} | OB_{100} | $H_{50} \text{ exp}^b$ (m) | $H_{50} \text{ calc}$ (m) |
|-----------------------|-------------------|-------------------|----------------------------|---------------------------|
| HNB | 0.01459 | 3.45 | 0.12 | 0.10 |
| PNA | -0.01015 | 1.89 | 0.15 | 0.14 |
| TETNB | -0.01899 | 0.78 | 0.27 | 0.20 |
| TETNA | -0.02698 | 0.37 | 0.41 | 0.25 |
| PA | -0.09484 | -0.44 | 0.87 | 1.10 |
| TNB | -0.11240 | -1.41 | 1.00 | 1.49 |
| TNAP | -0.09994 | -0.82 | 1.38 | 1.21 |
| TBN | -0.08907 | -1.68 | 1.40 | 1.03 |
| TNT | -0.11644 | -3.08 | 1.60 | 1.64 |
| TNA | -0.13033 | -1.75 | 1.77 | 1.93 |
| DATB | -0.16948 | -2.06 | 3.20 | 3.10 |
| TATB | -0.21440 | -2.33 | 4.90 | 4.81 |
| RDX | -0.02961 | 0.00 | 0.28 | 0.28 |
| HMX | -0.00953 | 0.00 | 0.32 | 0.20 |
| PETN | 0.02395 | 1.90 | 0.11 | 0.19 |
| NG | 0.02637 | 3.08 | 0.20 | 0.16 |
| 2# | -0.00696 | 2.52 | 0.11 | 0.11 |
| TNAZ | -0.06017 | 1.04 | 0.30 | 0.51 |
| CL-20 | 0.01550 | 1.37 | 0.20 | 0.17 |

^a The structures are depicted in Figure 1. ^b Data of H_{50} are taken from ref 12.

2. Factors Affecting the Impact Sensitivity of Nitro Compounds

For a nitro compound, its stability is dominated by the strength of its C–NO₂, N–NO₂, and O–NO₂ bonds. Zhang¹² pointed out that the strength of the above bonds could be scaled with the nitro group charge Q_{NO_2} , which is calculated by eq 2:

$$Q_{\text{NO}_2} = Q_{\text{N}} + Q_{\text{O}_1} + Q_{\text{O}_2} \quad (2)$$

where Q_{N} , Q_{O_1} , and Q_{O_2} are the net charges on the N and O atoms in the nitro group, respectively.

However, there is not a monotonic relationship between Q_{NO_2} and H_{50} , thus there may not be the same stability (or impact sensitivity) for those nitro compounds having equal nitro group

charge, or, vice versa, some nitro compounds with the same impact sensitivity did not have an equal nitro group charge. This fact, in our opinion, can be attributed to the difference in the oxygen balances among those nitro compounds. Of course, if only the oxygen balances are used to scale the impact sensitivity, it is still observed that the nitro compounds having equal oxygen balances did not have equal impact sensitivities. The above analysis implies that the nitro group charge and oxygen balances are two important factors affecting the impact sensitivity of nitro compounds, but neither of them can be used alone to quantify the impact sensitivity well.

The Q_{NO_2} or OB_{100} , we think, just expresses one part of the structural features influencing the impact sensitivity of nitro compounds. Hence, it is rational to employ both Q_{NO_2} and OB_{100} to correlate the impact sensitivity for nitro compounds.

In order to save CPU time and to quickly get the Mulliken net charges¹³ on the nitro groups of the nitro compounds, the semiempirical molecular orbital method (i.e., Austin Method 1)¹⁴ was employed. All the calculations were carried out by using the MOPAC suite of programs¹⁵ in an SGI workstation, and the options were set as the default during the calculation.

3. Results and Discussion

3.1. Building the Quantitative Model. In order to verify whether the above two parameters Q_{NO_2} and OB_{100} could be used to quantify the impact sensitivity H_{50} of a nitro compound, some nitrobenzenes and saturated nitro compounds whose impact sensitivities have been measured experimentally were collected, and their structural parameters Q_{NO_2} and OB_{100} were calculated (listed in Table 1). It should be mentioned that there might exist several different Q_{NO_2} values for the polynitro compounds. In this case, the Q_{NO_2} with the smallest absolute value was employed.

Correlating Q_{NO_2} and OB_{100} with experimental H_{50} for the compounds in Table 1, we obtained the following equation:

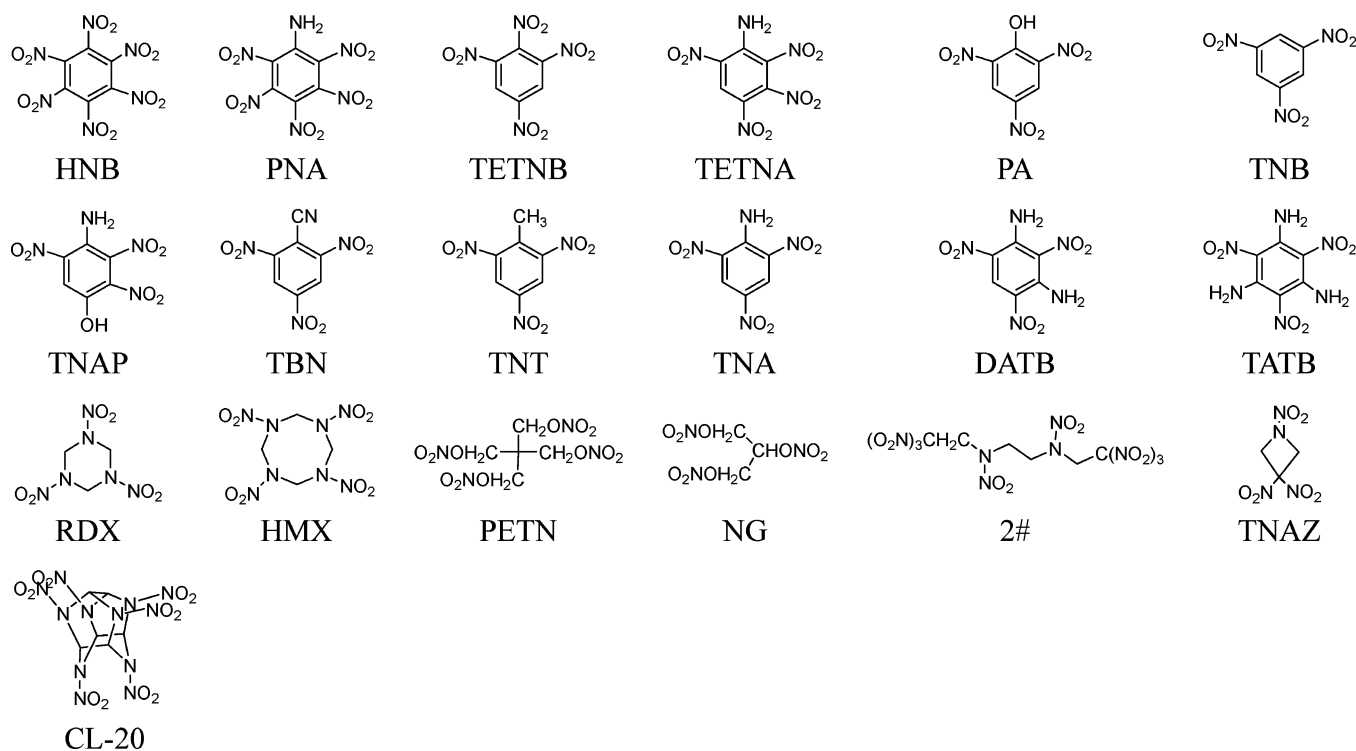


Figure 1. The structures of the compounds listed in Table 1.

$$H_{50} = -0.2418 - 20.45Q_{\text{NO}_2} + 0.1778\text{OB}_{100}$$

$$R = 0.9142, \text{SE} = 0.54 \text{ m}, n = 19, F = 41 \quad (3)$$

where, the statistics R , SE , n , and F denote the correlation coefficient, the standard error, the number of samples, and Fisher's F -statistic at the 95% probability level, respectively.

Generally, the quality of a correlation equation can be scaled in terms of the correlation coefficient R and its estimated standard error SE . The larger the R value and the smaller the SE value is, the better the quality of the correlation equation will be. The R and SE value of eq 3 indicated that the quality of the correlation equation is not good, and such a large estimated error is not accepted for practical purposes.

Using the square of the net charge of a nitro group (i.e., $Q_{\text{NO}_2^2}$) and OB_{100} as the parameters, we performed a regression analysis again for the same compounds in Table 1 and obtained eq 4:

$$H_{50} = 0.1926 + 98.64Q_{\text{NO}_2^2} - 0.03405\text{OB}_{100}$$

$$R = 0.9893, \text{SE} = 0.19 \text{ m}, n = 19, F = 367, \\ r_{\text{cv}} = 0.9853, s_{\text{cv}} = 0.21 \text{ m} \quad (4)$$

Compared with eq 3, the R and SE values of eq 4 are improved greatly by replacing the structural parameter Q_{NO_2} with its square, $Q_{\text{NO}_2^2}$. Figure 2 shows the plot of the experimental H_{50} versus the values estimated by eq 4, which visually indicate that the estimated H_{50} values for the nitro compounds agree well with the experimental ones. The estimation error by eq 4 is only 0.19 m, which is within the experimental bars.

A close examination of the coefficients in front of the structural parameters of eq 4 can provide physical insight to understand the structure–impact sensitivity relationship. In eq 4, the positive coefficient of $Q_{\text{NO}_2^2}$ implies that a molecule with large $Q_{\text{NO}_2^2}$ has a high H_{50} value and good stability. As is known, the larger the value of $Q_{\text{NO}_2^2}$ is, the higher the polarity of the bond attached to the NO_2 (e.g., $\text{C}-\text{NO}_2$, $\text{N}-\text{NO}_2$, $\text{O}-\text{NO}_2$, etc.) will be, hence the stronger the bond strength is and the more stable the molecule is. The negative coefficient of OB_{100} indicates that the values of H_{50} decrease as OB_{100} increases in a nitro compound, which is in agreement with Kamlet's suggestion.¹⁰

The aim of the establishment of a quantitative equation is not just to correlate the experimental H_{50} of compounds with their structures, but to more importantly predict the H_{50} for the

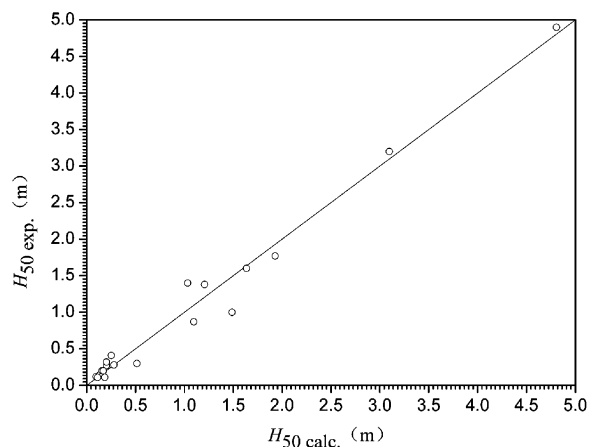


Figure 2. The plot of the calculated H_{50} values vs the experimental ones.

TABLE 2: The Predicted Impact Sensitivities for Some Nitro Compounds

| compound ^a | H_{50} pred. (m) | Q_{NO_2} | OB_{100} |
|-------------------------------------|--------------------|-------------------|-------------------|
| ONC | 0.18 | 0.03328 | 3.45 |
| TNPA | 0.38 | 0.05559 | 3.45 |
| TNA1 | 3.12 | -0.16702 | -5.06 |
| TEX | 0.22 | -0.00201 | -0.76 |
| DAMN | 1.67 | -0.11257 | -6.67 |
| H_3CNO_2 | 6.01 | -0.24163 | -1.64 |
| $\text{H}_2\text{C}(\text{NO}_2)_2$ | 1.72 | -0.12955 | 3.77 |
| $\text{HC}(\text{NO}_2)_3$ | 0.11 | -0.03492 | 5.96 |
| $\text{C}(\text{NO}_2)_4$ | 0.10 | 0.03892 | 7.14 |

^a Some of the structures are depicted in Figure 3.

compounds whose experimental impact sensitivities are still unavailable. Before a model is employed to predict the impact sensitivity H_{50} for nitro compounds other than those listed in Table 1, the stability and the predictive ability of the model must be assessed. It was suggested^{16,17} that the internal cross-validation method was a practical and reliable method for testing the significance and predictive ability of a model. Hence, the cross-validation using the leave-one-out (LOO) method is employed to test the predictive ability of eq 4.

During the LOO method procedure, each time, one molecule is removed from the training set, and a model is developed with the remaining $N - 1$ molecules. At each step, the H_{50} value of the removed molecule is to be predicted by the obtained model. This process is repeated until each molecule of the training set is predicted. In principle, the predictive ability of the model is quantified in terms of the corresponding LOO cross-validated parameters, r_{cv} and s_{cv} , which are defined as¹⁷

$$r_{\text{cv}}^2 = 1.0 - \frac{\sum_{i=1}^n (y_i - \hat{y}_i)^2}{\sum_{i=1}^n (y_i - \bar{y})^2} \quad (5)$$

$$s_{\text{cv}} = \sqrt{\frac{\sum_{i=1}^n (y_i - \hat{y}_i)^2}{N - D - 1}} \quad (6)$$

where y_i and \hat{y}_i are the experimental and predicted values, respectively, \bar{y} is the mean value of y_i , N is the number of samples to be used for building the model, and D is the number of descriptors in the model.

The r_{cv} and s_{cv} values indicated that eq 4 is stable, and its predicted accuracy for H_{50} of the nitro compound is within 0.21 m. Thus eq 4 can be recommended to predict the H_{50} for those nitro compounds whose experimental values are unmeasured.

3.2. Predicting the H_{50} Value for Some Nitro Compounds.

After finishing eq 4, we collected impact sensitivity index H_{50} values of pentanitrobenzene (0.11 m) and 2,3,4-trinitrotoluene (0.56 m) from the literature.¹⁸ Here we used eq 4 to predict their H_{50} values and obtained the H_{50} values 0.11 and 0.53 m, respectively, which were in agreement with the experimental values.

Because of the difficulties of the experiments, there are many nitro compounds whose impact sensitivities are still unmeasured. Here, we employed eq 4 to predicted H_{50} for some compounds (listed in Table 2). The reliability of the predicted results remains to be tested by further experiments.

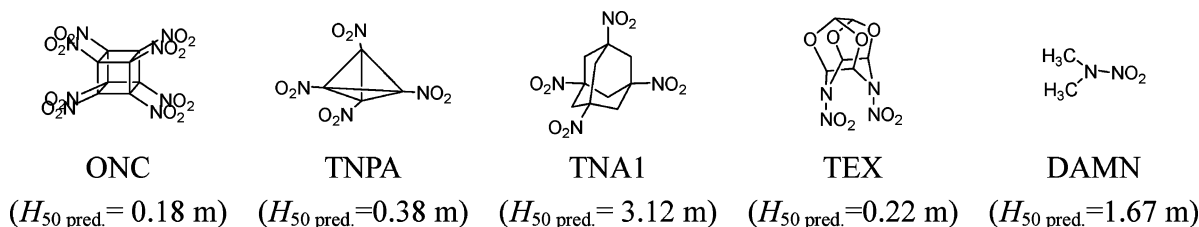


Figure 3. The structures of some of the compounds listed in Table 2.

As can be seen from the H_{50} values predicted by eq 4, the impact sensitivity of ONC, TNPA, and TNA1 increases in the order $\text{ONC} < \text{TNPA} < \text{TNA1}$.

It can be observed from the predicted H_{50} of nitromethanes (Table 2) that the stability of nitromethanes decreases as the number of nitro groups increases, which is in agreement with the chemical intuition and the trend predicted by Zhang.¹² Interestingly, when one of the H atoms of the CH_3NO_2 molecule was substituted by a NO_2 group, the impact sensitivity value H_{50} decrease sharply from 6.01 m of CH_3NO_2 to 1.72 m of $\text{CH}_2(\text{NO}_2)_2$. If the second H atom of CH_3NO_2 is substituted continuously by a NO_2 group, it will yield a very unstable molecule, $\text{CH}(\text{NO}_2)_3$, whose H_{50} is only 0.11 m. Meanwhile, the impact sensitivity value H_{50} decreases little from $\text{CH}(\text{NO}_2)_3$ to $\text{C}(\text{NO}_2)_4$. Zhang¹² ranked those compounds according to their stabilities, and pointed out that the decreasing order for H_{50} is as follows: $\text{CH}_3\text{NO}_2 > \text{CH}_2(\text{NO}_2)_2 > \text{CH}(\text{NO}_2)_3 > \text{C}(\text{NO}_2)_4$. The predicted stability order for those compounds by the present work agrees with that of Zhang's work.¹² However, Zhang¹² just semiquantitatively indicated the stability and did not calculate the specific H_{50} values of nitromethanes. In the present work, the impact stabilities are completely quantified. Of course, Rice¹⁸ recently pointed out that "the impact test is considered to provide only a crude, qualitative estimate of an explosive's sensitivity, and its results are often considered to be suspect." That is to say, since eq 4 was established from the experimental H_{50} values, the predicted H_{50} values with eq 4, perhaps, are not very accurate. However, the real value of eq 4 is that it provides new insight into understanding the effect of the molecular structure on impact sensitivity for the nitro compound, which is a useful indicator for evaluating the relative impact sensitivity of the mentioned nitro compounds. This work made good progress in the study of the structure–stability relationship of nitrobenzenes and saturated nitro compounds, and it may be helpful in HEDM design.

4. Conclusion

The oxygen balances and square of the nitro group charge are two important factors influencing the stability of nitro

compounds. Using these two structural parameters as variables, a good quantitative model was established for predicting the H_{50} values of nitrobenzenes and saturated nitro compounds with a 0.21 m error. The model of this work reveals that the impact sensitivity of a nitro compound must be judged by both the $Q_{\text{NO}_2}^2$ and OB_{100} values.

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