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Prediction of shock sensitivity of explosives based on small-scale gap test

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Abstract

A new method is described to predict shock sensitivity of $C_aH_bN_cO_d$ explosives without using any experimental data. It can determine shock sensitivity based on small-scale gap test as the pressure required to initiate material pressed to 90%, 95% and 98% of theoretical maximum density. Three essential parameters would be needed in the new scheme which contain $a + b/2 - d$, the existence of α -C–H linkage in nitroaromatic compounds or N–NO₂ functional group and difference of the number of amino and nitro groups attached to aromatic ring. Predicted shock sensitivities in some well-known explosives have a root mean square (rms) deviation of 3.97, 4.02 and 5.89 kbar of experiment to initiate pressure of material pressed to 90%, 95% and 98% of theoretical maximum density, respectively.

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1. Introduction

The study of energetic materials by theoretical methods has accelerated dramatically over recent years and has provided a considerable insight into the understanding of factors affecting their behavior. An ideal explosive can be considered as high performance energetic compound with sufficient insensitivity to permit safe handling. It should not be, at the same time, so insensitive that detonation becomes difficult or impractical. Fortunately, many empirical methods complemented the computer output can be used for desk calculations of performance [1]. Moreover, some new methods have recently been developed to predict detonation performance of ideal and non-ideal explosives [2]. As representative example, different procedures have been recently introduced for simple evaluation of heats of detonation using appropriate selection of decomposition products [3], gas phase heat of formation [4] and structural parameters [5].

Sensitivity of an explosive has been identified in terms of nature of stimuli causing detonation. Impact, shock, heat, electrostatic charge and friction are some of these which can cause detonation. Of these, impact and shock are two wellknown of many kinds of sensitivity so that vulnerability of an explosive to detonation caused by accidental impact or shock is one of the important factors in its assessing. Since the drop weight impact test is convenient and the most common method of assessing sensitivities, most of the studies that have attempted to associate molecular properties with sensitivities rely on drop weight impact measurements [6–46]. For example, some simple relationships have been found that relate impact sensitivities with measured and predicted molecular properties such as the oxygen balance of the molecules [6,7], molecular electronegativities [17,18] and recently elemental composition of pure explosives or through artificial neural network [43–46].

The gap test indicates the shock sensitivity of an explosive. A variety of gap tests have been used to qualitatively measure the shock wave amplitude required to initiate detonation in explosives, e.g. at Naval Surface Warfare Center (NSWC) and Los Alamos National Laboratory (LANL). A standard small-scale gap test [23] is often used to measure shock sensitivity. For shock

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initiated studies, the collection of information has been gathered by NSWC using Navy small-scale gap test [23]. The results of impact sensitivity are often not reproducible because factors in the impact experiment that might affect the formation and growth of hot spots could strongly affect the measurements but reliable shock sensitivity tests exist. Moreover, reported data of impact sensitivities are extremely sensitive to the conditions under which the tests are performed as well as all of impact sensitivity correlations can be applied only for pure energetic compounds [6–46]. There are the same questions about the mechanisms of initiation for both the impact harmer and shock tests.

Price [47] has considered a variety of factors important in shock wave sensitivity test. Storm et al. [23] have shown that there is a linear correlation between the impact and shock sensitivity under specified conditions for five energetic compounds with closely related structure, i.e. TNB, DIPAM, MATB, DATB and TATB. Since the results of impact sensitivity test depends on the conditions of the experiment, they used the impact sensitivity as measured at LANL and/or NSWC using the Bruceton method, type 12 tools, 2.5 kg weight, 40 mg sample, 5/0 sand paper and 25 trials. Owen et al. [15] also found that measured impact and shock sensitivities of seven polynitroaromatic molecule correlative with an approximation of the electronegativity potential at midpoint of the C–N bond for the longest C–NO₂ bond in each molecule.

Organic pure and mixed explosives can undergo very rapid and high exothermic reaction for which an understanding of sensitivity is in large part of chemical problem. The purpose of this work is to present a new method for reliable estimation shock sensitivity based on small-scale gap test as the pressure required for initiating material pressed to 90%, 95% and 98% of theoretical maximum density. Predicted results will be compared to measured data for three mentioned loading densities. The present procedure reveals a new correlation to predict shock sensitivity of explosives as an important factor to explosive users in industry. Moreover, it provides a simple pathway to determine safe handling of new pure and mixed energetic molecules.

2. Development of new correlation for small-scale gap thicknesses shock sensitivity

Due to sensitivity or performance problems through predictive capabilities at the early stages of development, elimination of any poor candidate is highly desirable to scientists and explosive industries. To predict various properties of a notional energetic material that are associated with the performance and sensitivity before expending resources in its synthesis, the development of new methods can help the chemists to develop systematic and scientific formulations of appropriate futuristic target molecules having important properties such as enhanced detonation performance and good sensitivity. Maximizing performance while minimizing sensitivity is highly desirable in designing and formulating of energetic materials because necessarily metastable and sensitive of them. Since small-scale shock sensitivities of various explosives depend on chemical structural parameters, the main object of this work was to find a good correlation that can be applied for explosives. Theoretical studies

of energetic materials have provided a considerable insight into understanding of factors affecting their behavior.

Sensitivity of an explosive is complex and its understanding is in large part of a chemical problem. Its tests are devised with the idea of judging the potential safety of use in a particular application. Several properties contribute to the materials' response to the stimulus in a sensitivity test, namely (a) the ease with which a detectable reaction of any kind can be initiated in an explosive; (b) the tendency of a small reaction, once established, to grow to destructive proportions; and (c) the ease with which a high-order detonation can be established in an explosive. However, they are a consequence of the kinetics and thermodynamics of the thermal decomposition of the explosive. The ease with which a detectable relation of any kind and a high-order detonation as well as tendency of a small reaction can be initiated and established are several properties in an explosive which response to the stimulus in a sensitivity test.

The study of shock sensitivity as measured by NSWC small-scale gap test shows that some special structural parameters may affect their values. We have found that three essential parameters have predominant effects which include distribution of oxygen between carbon and hydrogen to form carbon monoxide and water, the existence of nitramine groups or α -C–H linkage in nitroaromatic compounds and difference of the number of amino and nitro groups in aminoaromatic (Ar–NH₂) energetic compounds. However, the results have indicated that the following general equation can be applied for C_aH_bN_cO_d explosives:

$$P_{x\% \text{ TMD}} = x_1 + x_2(a + b/2 - d) + x_3 E_{\alpha\text{CH}/\text{NNO}_2}^0 + x_4(A n_{\text{NH}_2} - n_{\text{NO}_2})_{\text{pure}} \quad (1)$$

where $P_{x\% \text{ TMD}}$ is the pressure in kbar required to initiate material pressed to $x\%$ of theoretical maximum density (TMD), x_1 – x_4 are adjustable parameters which can be obtained by the best fit to experimental NSWC small-scale gap test shock sensitivities data for different C_aH_bN_cO_d explosives, $a + b/2 - d$ is a parameter that shows distribution of oxygen between carbon and hydrogen to form carbon monoxide and water, $E_{\alpha\text{CH}/\text{NNO}_2}^0$ a parameter that shows the existence of α -C–H linkage in nitroaromatic compounds or N–NO₂ functional group, $(A n_{\text{NH}_2} - n_{\text{NO}_2})_{\text{pure}}$ difference of the number of amino and nitro groups in aminoaromatic energetic compounds in which 'A' is constant. It should be mentioned that $E_{\alpha\text{CH}/\text{NNO}_2}^0 = 1$ for nitramines or α -C–H linkage in nitroaromatic compounds and has the zero value for energetic compounds in which N–NO₂ functional groups do not exist in their chemical structure. Since sensitivity of different class of explosives depends on oxygen content [6,7], the parameter $a + b/2 - d$ is a good factor for distribution of oxygen between carbon and hydrogen in detonation products. It is also found that the presence of N–NO₂ functional group can improve sensitivity of nitramine explosives. Therefore, we can expect that optimized coefficient of $E_{\alpha\text{CH}/\text{NNO}_2}^0$ has minus sign. Attachment of amino groups to aromatic ring may enhance stability of energetic compound. Since the delocalization of the π electrons in the aromatic ring is an important factor in the stability of aromatics, addition of electron withdrawing groups, NO₂ groups lead to a removal of the stabilization of the aromatic ring. In con-

Table 1

Comparison of predicted shock sensitivities of different common explosives and their mixtures with measured data [23] by the NSWC small-scale gap test for the pressure in kbar required to initiate material pressed to 90% of theoretical maximum density

Name ^a	(<i>P</i> _{90% TMD}) _{exp}	(<i>P</i> _{90% TMD}) _{Eq. (2a)}	Dev	(<i>P</i> _{95% TMD}) _{exp}	(<i>P</i> _{95% TMD}) _{Eq. (2b)}	Dev	(<i>P</i> _{98% TMD}) _{exp}	(<i>P</i> _{98% TMD}) _{Eq. (2c)}	Dev
PETN	7.47	10.00	−2.53	10.76	14.53	−3.77	13.69	18.82	−5.13
TNETB	9.25	5.48	3.77	13.13	9.57	3.56	17.48	14.40	3.08
RDX	10.97	10.48	0.49	15.77	15.60	0.17	20.35	21.29	−0.94
HMX	10.81	10.48	0.33	14.32	15.60	−1.28	17.49	21.29	−3.80
HNAB	12.77	21.32	−8.55	18.11	26.92	−8.81	22.48	29.87	−7.39
TETRYL	10.64	13.87	−3.23	15.14	19.32	−4.18	19.42	24.60	−5.18
TNEDV	14.99	15.66	−0.67	—	—	—	—	—	—
HNB	18.25	21.32	−3.07	—	—	—	—	—	—
TACOT-z	34.43	30.37	4.07	41.26	36.84	4.42	—	—	—
TNB	14.96	20.18	−5.22	27.28	25.68	1.60	37.25	28.76	8.49
DIPAM	25.11	23.58	1.53	29.71	29.40	0.31	33.04	32.08	0.96
TNT	17.72	18.39	−0.67	25.65	24.27	1.38	33.35	29.02	4.33
MATB	27.91	21.32	6.60	35.35	26.92	8.43	41.02	29.87	11.15
DATB	46.2	37.66	8.54	54.22	56.42	−2.20	59.88	70.80	−10.92
TATB	70.38	73.01	−2.63	121.92	121.24	0.68	164.86	161.50	3.36
PENTOLITE	8.21	11.14	−2.93	11.73	16.33	−4.60	15.18	21.94	−6.76
OCTOL-75/25	12.62	11.34	1.28	19.23	16.54	2.69	25.98	22.13	3.85
OCTOL-65/35	12.3	11.71	0.59	18.5	16.95	1.55	26.02	22.49	3.53
COMP B-3	16.15	12.01	4.14	21.54	17.28	4.26	27.76	22.79	4.97
HNS	26.26	28.10	−1.84	30.15	34.36	−4.21	32.9	36.50	−3.60
rms deviation			3.97			4.02			5.89

^a See Appendix A for glossary of compound names.

trast, amino groups partially counteract the electron withdrawing effect of nitro groups which enhance the stabilization of aromatic ring [27]. However, the parameter $(An_{NH_2} - n_{NO_2})_{pure}$ is useful variable to show extra stability due to increasing the number of amino groups attached to aromatic ring in which constant ‘A’ shows the contribution of stability effect of amino groups with respect to removal of stabilization of aromatic ring. Moreover, the contribution of term $(An_{NH_2} - n_{NO_2})_{pure}$ is valid for its positive values. We can also expect that optimized coefficient of this parameter has positive sign in Eq. (1). To obtain adjustable parameters, we have used a database given by Storm et al. [23], where the experimental data of *P*_{90%TMD}, *P*_{95%TMD} and *P*_{98%TMD} of different well-known explosives have been collected. Multiple linear regression method [48] was used to find adjustable parameters. Since the equation set is overdetermined [48], the left-division method for solving linear equations uses the least squares method. The optimized correlations for *P*_{90%TMD}, *P*_{95%TMD} and *P*_{98%TMD} can be given as follows:

$$\begin{aligned}
 P_{90\%TMD} \text{ (kbar)} = & 16.790 + 2.2625(a + b/2 - d) \\
 & - 6.3142E_{NNO_2}^0 \\
 & + 17.719(1.93n_{NH_2} - n_{NO_2})_{pure} \quad (2a)
 \end{aligned}$$

$$\begin{aligned}
 P_{95\%TMD} \text{ (kbar)} = & 21.964 + 2.4792(a + b/2 - d) \\
 & - 6.3677E_{NNO_2}^0 \\
 & + 32.921(1.93n_{NH_2} - n_{NO_2})_{pure} \quad (2b)
 \end{aligned}$$

$$\begin{aligned}
 P_{98\%TMD} \text{ (kbar)} = & 25.449 + 2.2106(a + b/2 - d) \\
 & - 4.1620E_{NNO_2}^0 \\
 & + 46.392(1.93n_{NH_2} - n_{NO_2})_{pure} \quad (2c)
 \end{aligned}$$

Experimental data of Table 1 were used to find adjustable coefficients of Eqs. (2). *R*-squared values or the coefficients of determination of Eqs. (2a), (2b) and (2c) are 0.929, 0.974 and 0.970, respectively [48]. However, the new correlations, which are based on some physical and structural parameters, show surprisingly very good agreement with experimental values. As seen, Eqs. (2a)–(2c) requires no prior knowledge of any measured physical, chemical or thermochemical properties of explosive. Calculated shock sensitivities are given in Table 1 and compared with corresponding measured values [23]. Eqs. (2a)–(2c) provide a new simple empirical available method to find reliable estimation of small-scale of shock sensitivity. Since a small particle size can reduce shock sensitivity at high density, it can be expected that percent of deviations of Eqs. (2) becomes large for very fine particle size.

3. Conclusions

Prediction of sensitivity of an energetic compound is one of the essential parameters of somewhat more practical importance to the explosive user. The present method can act as predictive tools for estimating small-scale gap test of $C_aH_bN_cO_d$ explosives. The present method may be appealing and the results are very promising because it requires as input only three structural parameters of energetic compounds. The new method provides the simplest procedure for hand calculation of shock sensitivity of energetic compounds. There are no high percentage errors in shock sensitivity predictions as compared to large uncertainty in different methods of impact sensitivity predictions. However, comparison of calculated results with experimental data listed in Table 1 may be taken as appropriate validation of Eqs. (2a) and (2b) for use with $C_aH_bN_cO_d$ explosives.

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Appendix A. Glossary of compound names

1. COMP B-3: 60/40 RDX/TNT ($C_{2.04}H_{2.50}N_{2.15}O_{2.68}$)
2. DATB: 1,3-diamino-2,4,6-trinitrobenzene ($C_6H_5N_5O_6$)
3. DIPAM: 3,3'-diamino-2,2',4,4',6,6'-hexanitrobiphenyl ($C_{12}H_6N_8O_{12}$)
4. HMX: cyclotetramethylenetetranitramine ($C_4H_8N_8O_8$)
5. HNAB: 2,2',4,4',6,6'-hexanitroazobenzene ($C_{12}H_4N_8O_{12}$)
6. HNB: hexanitrobenzene ($C_6N_6O_{12}$)
7. HNS: 2,2',4,4',6,6'-hexanitrostilbene ($C_{14}H_6N_6O_{12}$)
8. OCTOL-75/25: 75/25 HMX/TNT ($C_{1.78}H_{2.58}N_{2.36}O_{2.69}$)
9. OCTOL-65/35: 65/35 HMX/TNT ($C_{1.96}H_{2.53}N_{2.22}O_{2.68}$)
10. PENTOLITE: 50/50 TNT/PETN ($C_{2.33}H_{2.37}N_{1.29}O_{3.22}$)
11. PETN: pentaerythritoltetranitrate ($C_5H_8N_4O_{12}$)
12. RDX: cyclomethylenetrinitramine ($C_3H_6N_6O_6$)
13. TACOT-z: 1,3,7,9-tetranitrodibenzo-1,3a,4,6a-tetraazapentalene ($C_{12}H_4N_8O_8$)
14. TATB: 1,3,5-triamino-2,4,6-trinitrobenzene ($C_6H_6N_6O_6$)
15. TETRYL: *N*-methyl-*N*-nitro-2,4,6-trinitroaniline ($C_7H_5N_5O_8$)
16. TNB: trinitrobenzene ($C_6H_3N_3O_6$)
17. TNEDV: trinitroethyl-4,4-dinitrovalerate ($C_7H_9N_5O_{12}$)
18. TNETB: trinitroethyltrinitrobutrate ($C_6H_6N_6O_{14}$)
19. TNT: 2,4,6-trinitrotoluene ($C_7H_5N_3O_6$)
20. MATB: 2,4,6-trinitroaniline ($C_6H_4N_4O_6$)

References

- [1] A.K. Sikder, G. Maddala, J.P. Agrawal, H. Singh, J. Hazard. Mater. A 84 (2001) 1.
- [2] M.H. Keshavarz, A simple theoretical prediction of detonation velocities of non-ideal explosives only from elemental composition, in: P.B. Warey (Ed.), New Research on Hazardous Materials, Nova Science Publishers Inc., 2006 (Chapter 8).
- [3] M.H. Keshavarz, H.R. Pouretedal, Thermochim. Acta 414 (2004) 203.
- [4] M.H. Keshavarz, Thermochim. Acta 428 (2005) 95.
- [5] M.H. Keshavarz, J. Hazard. Mater. A, in press.
- [6] M.J. Kamlet, Proceedings of the Sixth Symposium (International) on Detonation, Office of the Chief of Naval Operations, Coronado, CA, Washington, DC, 1976, p. 312.
- [7] M.J. Kamlet, H.G. Adolph, Propell. Explos. 4 (1979) 30.
- [8] A. Delpuech, J. Cherville, Propell. Explos. 3 (1978) 169.
- [9] A. Delpuech, J. Cherville, Propell. Explos. 4 (1979) 61.
- [10] A. Delpuech, J. Cherville, Propell. Explos. 4 (1979) 121.
- [11] M.J. Kamlet, H.G. Adolph, Proceedings of the Seventh Symposium (International) on Detonation, Annapolis, Maryland, 1981, p. 84.
- [12] H.G. Adolph, J.R. Holden, D.A. Cichra, Technical Report NSWC TR 80-495, Naval Surface Weapons Center, Dahlgren, VA, 1981.
- [13] P. Politzer, L. Abrahmsen, P. Sjöberg, J. Am. Chem. Soc. 106 (1984) 855.
- [14] P. Politzer, P.R. Laurence, L. Abrahmsen, B.A. Zilles, P. Sjöberg, Chem. Phys. Lett. 111 (1984) 75.
- [15] F.J. Owens, K. Jayasuriya, L. Abrahmsen, P. Politzer, Chem. Phys. Lett. 116 (1985) 434.
- [16] I. Fukuyama, T. Ogawa, A. Miyake, Propell. Explos. Pyrotech. 11 (1986) 140.
- [17] J. Mullay, Propell. Explos. Pyrotech. 12 (1987) 60.
- [18] J. Mullay, Propell. Explos. Pyrotech. 12 (1987) 121.
- [19] S.R. Jain, Propell. Explos. Pyrotech. 12 (1987) 188.
- [20] C.M. Traver, L.E. Fried, A.J. Rigger, D.F. Calef, Proceedings of the Seventh Symposium (International) on Detonation, Snowmass, Colorado, 1988, p. 49.
- [21] J.S. Murray, P. Lane, P. Politzer, P.R. Bolduc, Chem. Phys. Lett. 168 (1990) 135.
- [22] W.S. Wilson, D.E. Bliss, S.L. Christian, D.J. Knight, Naval Weapons Center Technical Report NWC TP 7073, 1990.
- [23] C.B. Storm, J.R. Stine, J.F. Kramer, in: S.N. Bulusu (Ed.), Chemistry and Physics of Energetic Materials, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1990, pp. 605–639.
- [24] P. Politzer, J.S. Murray, P. Lane, P. Sjöberg, H.G. Adolph, Chem. Phys. Lett. 181 (1991) 78.
- [25] G.T. Afanas'ev, T.S. Pivina, D.V. Sukhachev, Propell. Explos. Pyrotech. 18 (1993) 309.
- [26] L.E. Fried, A.J. Ruggiero, J. Phys. Chem. 98 (1994) 9786.
- [27] J.S. Murray, P. Lane, P. Politzer, Mol. Phys. 85 (1995) 1.
- [28] P. Politzer, J.S. Murray, Mol. Phys. 86 (1995) 251.
- [29] P. Politzer, J.S. Murray, J. Mol. Struct. 376 (1996) 419.
- [30] P. Politzer, J.S. Murray, in: P.L. Markinas (Ed.), Organic Energetic Compounds, Nova Science Publishers, New York, 1996.
- [31] J. Fan, H. Xiao, J. Mol. Struct. (THEOCHEM) 365 (1996) 225.
- [32] F.J. Owens, Mol. Struct. (THEOCHEM) 370 (1996) 11.
- [33] K.L. McNesby, C.S. Coffey, J. Phys. Chem. B 101 (1997) 3097.
- [34] M. Vaullerlin, A. Espagnacq, L. Morin-Allory, Propell. Explos. Pyrotech. 23 (1998) 237.
- [35] H.-M. Xiao, J.-F. Fan, Z.-M. Gu, H.-S. Dong, Chem. Phys. 226 (1998) 15.
- [36] J. Fan, Z. Gu, H. Xiao, H. Dong, J. Phys. Org. Chem. 11 (1998) 177.
- [37] J.S. Murray, P. Lane, P. Politzer, Mol. Phys. 93 (1998) 187.
- [38] A.V. Belik, V.A. Potemkin, S.N. Sluka, Combust. Explos. Shock Waves 35 (1999) 562.
- [39] P. Politzer, H.E. Alper, in: J. Leszczynski (Ed.), Computational Chemistry, Reviews of Current Trends, vol. 4, World Scientific Publishing Co., Singapore, 1999.
- [40] C. Zhao-Xu, X. Heming, Int. J. Quantum Chem. 79 (2000) 350.
- [41] S. Zeman, Propell. Explos. Pyrotech. 25 (2000) 66.
- [42] B.M. Rice, J.J. Hare, J. Phys. Chem. A 106 (2002) 1770.
- [43] S.G. Cho, K. Tai No, E.M. Goh, J.K. Kim, J.H. Shin, Y.D. Joo, S. Seong, Bull. Korean Chem. Soc. 26 (2005) 399.
- [44] M.H. Keshavarz, H.R. Pouretedal, J. Hazard. Mater. A 124 (2005) 27.
- [45] M.H. Keshavarz, M. Jaafari, Propell. Explos. Pyrot. 31 (2006) 216.
- [46] M.H. Keshavarz, H.R. Pouretedal, A. Semnani, J. Hazard. Mater. A, in press.
- [47] D. Price, J. Energetic Mater. 3 (1985) 239.
- [48] W.J. Palm III, Matlab for Engineering Applications, WBC/McGraw-Hill, 1999, p. 339, 227.