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Stress-induced activation of decomposition of organic explosives: a simple way to understand

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Abstract We provide a very simply way to understand the stress-induced activation of decomposition of organic explosives by taking the simplest explosive molecule nitromethane (NM) as a prototype and constraining one or two NM molecules in a shell to represent the condensed phrase of NM against the stress caused by tension and compression, sliding and rotational shear, and imperfection. The results show that the stress loaded on NM molecule can always reduce the barriers of its decomposition. We think the origin of this stress-induced activation is due to the increased repulsive intra- and/or inter- molecular interaction potentials in explosives resulted from the stress, whose release is positive to accelerate the decomposition. Besides, by these models, we can understand that the explosives in gaseous state are easier to analyze than those in condensed state and the voids in condensed explosives make them more sensitive to external stimuli relative to the perfect crystals.

Keywords Decomposition of explosives · Loading condition · Stress-induced activation

Introduction

Security is an unavoidable topic in the field of explosives. It is evaluated in general by the so-called sensitivities of explosives which are the responses to external stimuli such as impact, shock, heat, electrostatic spark, and so forth. For any explosive applied under certain conditions, it is just its acceptable sensitivities that guarantee its applicability. Numerous research works on the sensitivities have been carried out experimentally and theoretically. Among them, the structure-sensitivity correlations of explosives have shown increasing interest and attracted much attention, in that they are indeed helpful for deep insights into the sensitivity mechanisms and reasonable design of new explosives.

Without respect to loading conditions, many correlations of explosives have been established on the basis of the characteristics of gaseous molecules (for example, geometry, energy and electronic structure) and crystal packings (for example, electronic structure), and the experimental sensitivities [1]. The indexes adopted in the correlations include: for single molecules, the strength of the weakest bonds described as bond length, bond order or bond dissociation energy (BDE) [2–6], the charges on active groups such as NO_2 and N_3 groups whose detachment triggers the molecular decomposition [7, 8], charge distribution [9], molecular electrostatic potentials [10], ^{13}C and ^{15}N NMR chemical shifts [11], the interaction energy among substituents around a same molecular skeleton [12], the energy gap of LUMO-HOMO [1], and the barrier for a rate-controlled reaction overcoming to take place [13]; and for crystals, the band gap in general [14, 15].

Because the so-called sensitivities are in nature determined by not only the internal structures of explosives but also the styles of external stimuli loading on them, it is important to elucidate accurately the structures by considering loaded conditions at the same time. In other words, the sensitivities are after all of loaded conditions but not of a common condition (no loading). Therefore, there should be great progress in understanding the sensitivities in terms of their condensed structures and the external stimuli loading on them including high temperature and pressure, shock, shear, charge, radiation, and so forth. For instance, Reed et al. confirmed that dynamical effects have a more significant effect on the band gap than static effects including hydrostatic stress, uniaxial strain, and shear strain, after investigating on the compressed nitromethane (NM) [16].

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Kuklja et al. also found there is a large decrease of band gap in shear-slid and unrelaxed 1,1-diamino-2,2-dinitroethylene (FOX-7). Also, Kuklja and his colleagues gave a good beginning for studying the strain-induced chemistry of the decomposition of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) and FOX-7. They provided a reasonable explanation on the much higher impact sensitivity of FOX-7 than that of TATB, due to the much lowered barrier of C-Nitro bond break induced by shear strain for FOX-7 [17, 18]. In addition, we concluded that there is a relationship between the sensitivities and the molecular stacking in crystal packing of explosives, and the desensitizing mechanisms of crystal graphite and TATB, and amorphous olefin, are all attributed to their good lubricating properties, or their very small stress-strain ratios caused by shear in contrast to those of primary explosives such as HMX, RDX, and so forth [19–22].

It is of great importance to investigate the dynamic behaviors of explosives under the conditions such as high temperatures and pressures to mimics explosives against actual external stimuli. The notable work is of the decomposition reactions at high temperatures and pressures derived from the *ab initio* molecule dynamic (CPMD) and molecular reaction field calculations. For example, Manaa et al. reported density functional molecular dynamic simulations to determine the early chemical events of hot (T= 3,000 K) and dense (ρ=1.97 g/cm^3, V/V_0=0.68) NM and confirmed some inter- or intra-molecular reactions [23]. Goddard's group extended a reactive force field ReaxFF to carry out molecular dynamics (MD) simulations on hexahydro-1,3,5-trinitro-1,3,5- triazine (RDX) and to study its shock-induced chemistry and found the decompositions products are different when RDX against shock with different impact velocities [24]. Also, Manaa et al. gave a mechanism for forming a nitrogen-rich molecule after TATB detonation using multiscale methods [25]. Because these dynamic reaction mechanisms included in condensed explosives are practically more related to the sensitivity mechanisms than to the static ones, we think it could be a new tendency to explore explosive sensitivity mechanisms by considering more and more the influences of dynamic factors.

However, currently, a common computer or station cannot finish these dynamic calculations soon due to their large requirements of time and computational resource consumption. From another side, we carried out some very simple and little time-consumed calculations to understand the stress-induced activation of decomposition of explosives. It therefore becomes an innovation of this paper, i.e., it can be enough to demonstrate some natures of condensed explosives under the loaded conditions even though it has very cheap calculations. Of course, the above mentioned dynamic calculations are also encouraged and should be performed conditionally, in that they can provide more details.

Methods

NM is the simplest nitro organic compound and has been taken as a prototype of explosives in many research works. Also, it was employed as the interested object in our calculations. As shown in the figures of the next section, we constrained one or two NM molecules in a shell and varied the volume of the shell (for NM monomer) or the inter-shell positions and orientations (for NM dimer) to mimic NM under stress conditions including tension, compression, sliding and rational shear, as well as imperfection. That is, comparing a fully-relaxed NM molecule without internal stress, these NM monomers and dimers in shells were unrelaxed or partly-relaxed and were therefore loaded with internal stress.

It is known that detonation initiation of explosives can proceed via some channels such as the rupture of a trigger linkage (for example, the weakest bonds in explosives such as C-NO$_2$, N-NO$_2$ and O-NO$_2$), the atom transfer (for example, hydrogen transfer), the isomerization (for example, nitro-nitrite isomerization), and so forth [13, 26–30]. Here we only pay attention to the break of C-N bond in NM, which is usually regarded as the most possible initiation of the NM decomposition [30]. The stress-induced activation of NM decomposition is accordingly represented by the energy change after the detachment of NO$_2$ from the shell or the bond dissociation energy (BDE) of C-N. All structure and energy calculations were performed using general gradient approximation (GGA) theory with Perdew-Burke-Ernzerhof (PBE) functions and a basis set of double-numeric quality basis with polarization functions (DNP) in Acceryls' code Dmol^3 [31–33]. In all calculations, NM molecule derived from an initial full relaxation was constrained and its rupture products, NO$_2$ and CH$_3$, could be relaxed or unrelaxed if necessary. The modeling for all cases will be detailed in the next section for a reading convenience and is not mentioned in this section.

Results and discussion

Tension and compression

Firstly, a simple case, only the elongation and the shortening of C-N bond is considered. Obviously, the stress-induced energy is only stored in the C-N bond. In this case, the ratio of the changed C-N bond length to the primary one corresponding to a fully relaxed NM molecule, L/L_0, is an indicator for stress. As illustrated in Fig. 1, BDE decreases with the increasing of distance deviated from the balance point (L/L_0=1). Because the increased energy caused by the stress, the elongation or the shortening of C-N bond, is fully contributed to BDE, the change tendency of BDE is just reverse to the potential energy surface (PES) of C-N bond:

Fig. 1 BDE-L/L$_0$ dependence of NM. L$_0$ and L are the C-N bond length of the fully relaxed NM and a changed C-N bond length, respectively. The red ←→and → ← denote the elongation and the shortening of C-N bond, respectively. Purple shells denote the constrained molecules. It is the same as the following
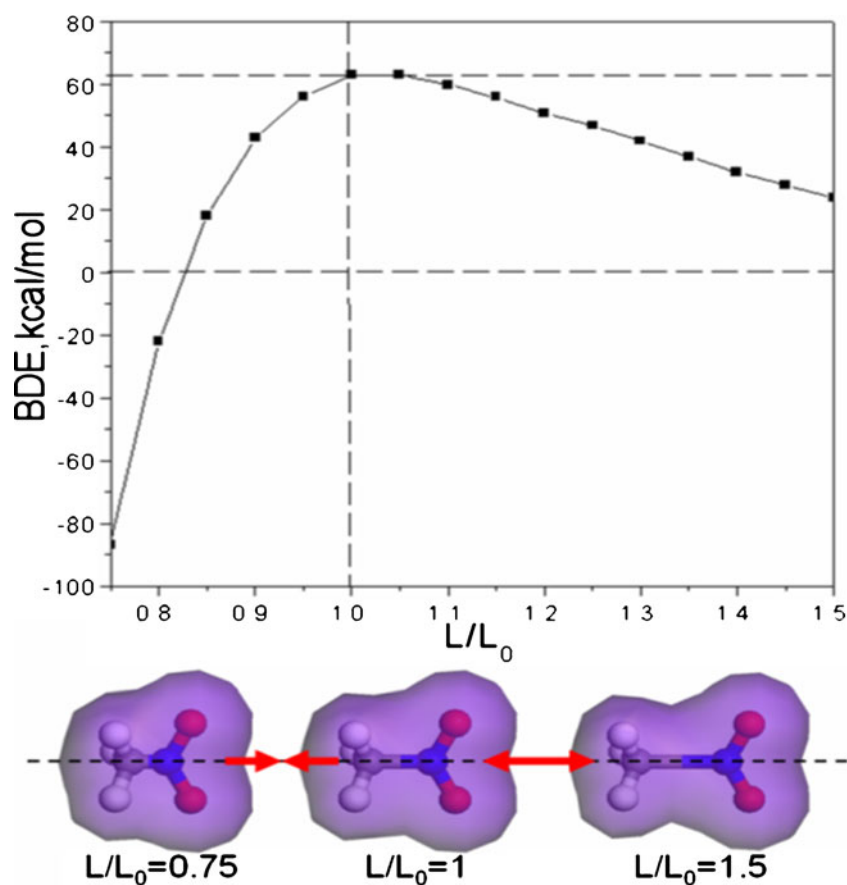
the more the stress-induced potential energy, the less the BDE. As to the negative value of BDE, it only implies that stress-induced potential energy stored on the C-N bond is already enough to break the C-N bond when it releases. Because the V is proportional to L^3 if the NM molecule is uniformly compressed or expanded, V/V$_0$ (or (L/L$_0$)^3) is equal to 0.53 on the zero point of the BDE where L/L$_0$= 0.81, corresponding to a threshold pressure against the stress leading to the decomposition or detonation of NM. Also, BDE tends to zero with L/L$_0$ tending to a high value. Additional energy is unnecessary to break the C-N bond in that it is already dissociated here. We can find from above discussion that the stress induced by the compression or tension of the C-N bond increases the internal energy of NM and makes the rupture of the C-N bond easier relative to the equilibrium NM whose internal stress is zero. This result is somewhat similar to that of Kohno et al.'s simulations on HMX, as they found the compressed N-N bonds can play two roles in physical stimuli: one being the energy storage for the explosion and the other being to serve as "hot spots in a molecule" [34]. As a matter of fact, energy is stored in both the compressed and the elongated C-N bond of NM, helpful for the NM decomposition and the formation of hot spots. The assumed compression and elongation of C-N bond can correspond to the cases of explosives against the stimuli of heat and mechanics, respectively.

Next, we discuss the effect of stress induced by the uniform compression and expansion of NM molecule on BDE. In this case, the ratio of the variation of molecular volume (V/V$_0$) represents the internal stress, which is zero when V/V$_0$=1. All four curves in Fig. 2 display the same trend: the more deviation from the balanced point (V/V$_0$= 1), the more BDE decreased. Because the increased external energy causing the increased internal stress is accumulated on all bonds of the molecule, it will release and be positive to break C-N bond during the NM decomposition. The difference among the four curves is attributed to the degree of energy release, that is, for any V/V$_0$: (1) when both NO$_2$ and CH$_3$ are relaxed, denoting all the accumulated energy releases, the required BDE is the least; (2) when neither NO$_2$ nor CH$_3$ is relaxed, denoting only the energy accumulated on C-N bond releases, the required BDE is the most among the four cases; and (3) when only NO$_2$ or CH$_3$ is relaxed, this case is between (1) and (2). Obviously, for any V/V$_0$, the sum of BDE of the cases of both NO$_2$ and CH$_3$ relaxed and neither of them relaxed is equal to that of only NO$_2$ relaxed and only CH$_3$ relaxed.

The cases of the full relaxation and unrelaxation of NO$_2$ and CH$_3$ can represent two extremes in the initial reaction of condensed NM. One is of no space for relaxation and another is of enough space. The practical cases should be between them. For example, for a compressed explosive
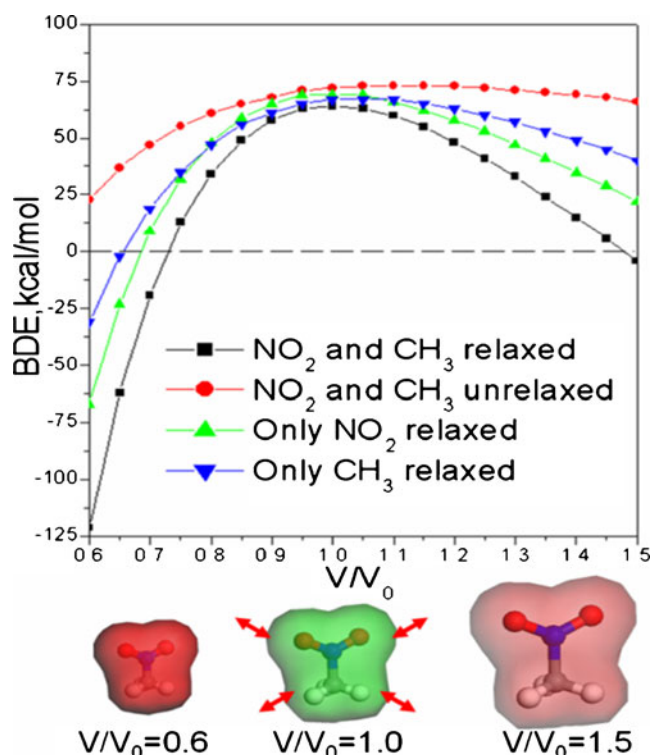
Fig. 2 BDE-V/V_0 dependence of NM. V_0 and V is the molecular volume of the fully relaxed and a changed NM, respectively. *Red ↔* shows the uniform compression and the uniform expansion of NM molecule. The *red* and *green* shells denote NM molecules with and without internal stress, respectively
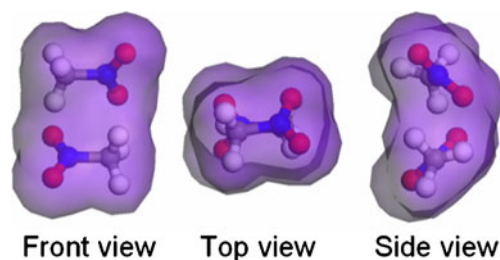

Fig. 3 Views along different orientations of the *initial* NM dimer for sliding-shear and rotational-shear calculations. The *initial* only denotes a position corresponding to $D_s=0$ or $\theta_r=0$, and not a point of a local minimum of energy necessarily. Two NM molecules in the dimer were arranged in parallel and their NO_2 and CH_3 groups are overlaid mutually. In the modeling of sliding-shear and rotational-shear, the top NM molecule slides along its C-N bond and rotates around a line vertical to its C-N bond and through the centriod of its C and N atoms, respectively. The distance between double C-N bonds is 3.0 Å

crystal, there is only very limited space for the relaxation of the ruptured groups; for thermally expanded explosive crystal, there should be much more space for the relaxation. Politzer et al. discussed the possibility of a correlation between the impact sensitivities of energetic compounds and the space available to their molecules in their crystal packing, and confirmed the impact sensitivities of some explosives are related to their volume differences, $\Delta V = V_{eff}–V(0.003)$ [35]. In fact, these volume differences can in a certain range reflect the stress-strain ration of the explosives, which can influence their impact sensitivities.

This can be extended to explain the effect of voids in condensed explosives on BDE. As pointed out above, the fuller relaxation of the broken NO_2 or CH_3 group leads to the lower BDE, suggesting the easier partition of C-N bond. In contrast to perfect crystal, the voids in crystal should make the fuller relaxation. As mentioned above, the zero value of BDE is suggested to be an initiation of C-N bond break, the corresponding volume strain V/V_0 is accordingly a threshold strain, below which the decomposition starts. According to the calculated results (partly shown in Fig. 2), we can find that: if both NO_2 and CH_3 group are fully relaxed, the corresponding threshold strain is $V/V_0=0.7$; if both NO_2 and CH_3 group are unrelaxed, the corresponding threshold strain is $V/V_0=0.5$; and if only NO_2 or CH_3 group

is relaxed, the corresponding threshold strain is $V/V_0=0.65$. It indicates the voids make the fuller relaxation, the higher threshold strain, namely, the easier decomposition. In general, people think the temperature of the gas in the voids increases when explosives suffer compression, useful to the formation of hot spots. According to our results, the hot spot can still form more readily around the voids even though
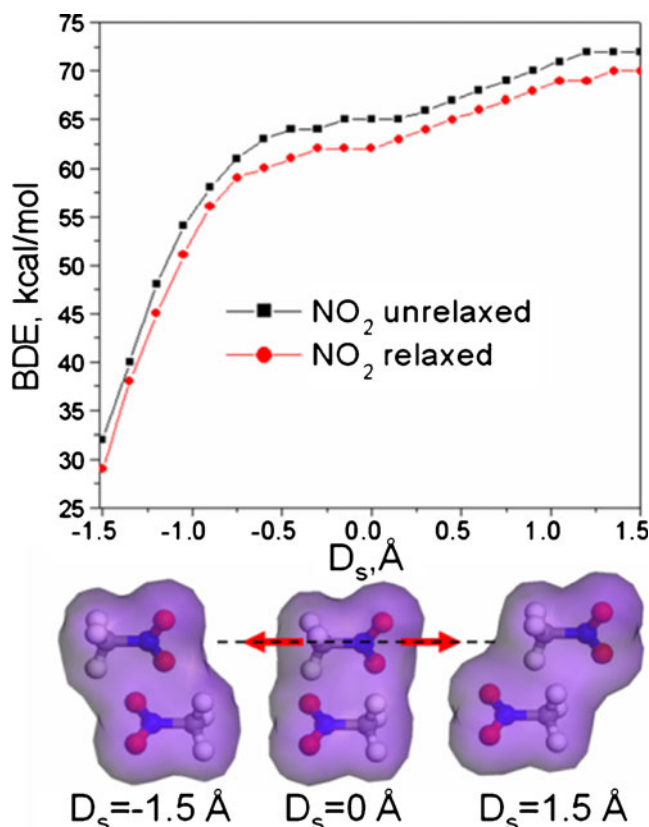

Fig. 4 BDE-D_s dependence of NM. BDE is the energy difference after the detachment of the top NO_2 group from the shell, and D_s is the slide distance

there is no gas closed in the voids, due to the lower BDE relative to the perfect crystal. This means the so called voids make explosives more sensitive to external stimuli.

Sliding and rotational shear

We arranged two NM molecules appositely on a point as illustrated in Fig. 3: the two molecules are parallel to each other along their C-N bonds, and their NO_2 and CH_3 groups are overlaid mutually. It is unnecessary to arrange the NM dimer to another point of a local minimum of energy because this kind of point of random can be enough to represent a stress-induced case. We selected the energy change after the departure of the NO_2 group of the top NM molecule from the shell as BDE.

The results of sliding shear are shown in Fig. 4. In the range of all sliding shear, that is, in the top NM molecule sliding 3 Å along its C-N bond, the variation of BDE shows the shear stress-induced activation of NM decomposition: the BDE changes from 29 to 70 $kcalmol^{-1}$ (NO_2 relaxed), or 32 to 72 $kcalmol^{-1}$ (NO_2 unrelaxed). In this case, the configuration of NM molecule is fixed. That is to say, the sliding shear-induced energy is stored as the increased intermolecular potentials, which are partly contributed to the break of the C-N bond. The internal stress is in principle the increased repulsive intermolecular potentials, implying that the C-N bond break can reduce the intermolecular repulsion, or the internal shear stress. From the configurations of the NM dimers, we can find that the repulsion of double oxygen atoms of different NO_2 groups (NO_2-NO_2 repulsion) in the case of $D_s=-1.5$ Å results in the more increased potential than those of $D_s=0$ and 1.5 Å. Kuklja et al. [17] concluded that the FOX-7 possesses higher impact sensitivity than TATB due to its lowered BDE during its interlayer sliding shear. This lowering of BDE is in principle resulted from the large repulsion between neighboring layers, but this repulsion in TATB is very small.

The case of rotational shear shown in Fig. 5 is similar to that of sliding shear. After a rotation of 180°, the BDE changes within 56 to 68 $kcalmol^{-1}$ (NO_2 relaxed), or 58 to 71 $kcalmol^{-1}$ (NO_2 unrelaxed). It confirms that the stress induced by rotational shear can make the C-N bond easier to break. The BDE difference in all cases, namely, different BDE corresponding to different position and orientation, is attributed to the difference of the increased repulsive potentials caused by the shear stress.

In both above cases, the BDE will decrease much more when we shorten the distance between the double C-N bonds of two NM molecules, and vice versa. It is attributed to the difference of intermolecular potential resulted from the shear. Furthermore, comparing the most BDEs shown in Figs. 1, 3 and 4, we can find the most BDE of a single NM molecule is higher than that of its dimer. It implies the more difficult decomposition of condensed explosives than that of
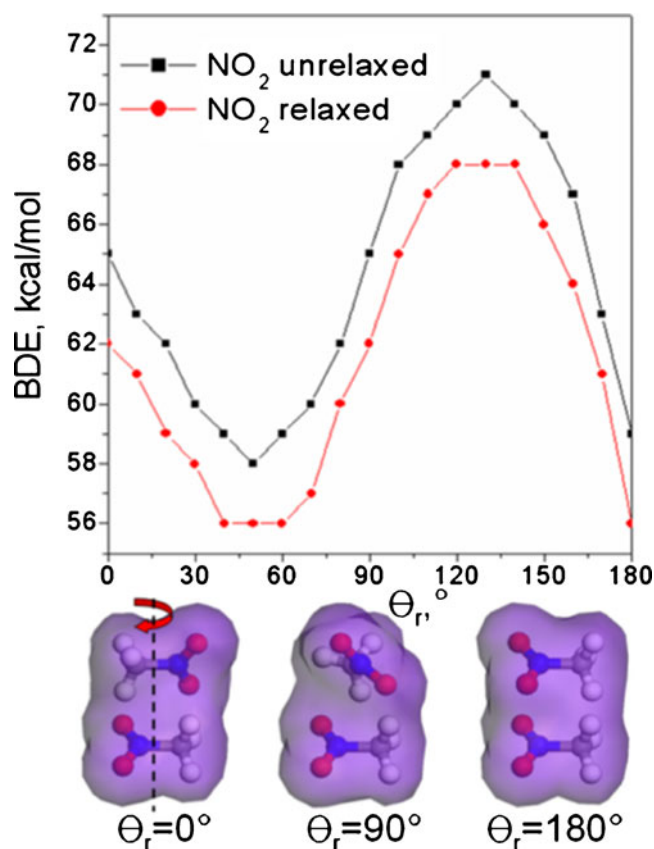

Fig. 5 BDE-θ_r dependence of NM. BDE is the energy difference after the detachment of the top NO_2 group from the shell, and θ_r is the rotated degree
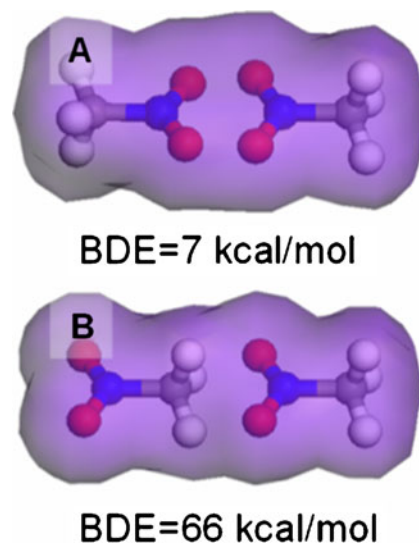

Fig. 6 Plot showing the decrease of BDE due to molecular dislocation. **a** and **b** denote the contact modes of NO_2-to-NO_2 and NO_2-to-CH_3, respectively. The distance between double N atoms in (**a**) is 3.114 Å and the distance between neighboring C and N atoms belonging respectively to the two NM molecules in B is 3.0 Å. Two C-N bonds are on a same line in both cases

gaseous explosives, which agrees with Kuklja et al.'s calculated BDEs of $C-NO_2$ of isolated molecules and of the molecules in crystals of TATB and Fox-7, 71 and $100-107$ $kcal\,mol^{-1}$, and 71 and 92 $kcal\,mol^{-1}$, respectively [17].

Imperfection

A case of stress induced by imperfection, molecular dislocation, is taken into account. From the practical crystal packing of NM, we can find that the two neighboring molecules in it tend to arrangement like Fig. 6b. As shown in Fig. 6a, we suppose a defect induced by a reversed-orientation NM molecule. That is, the contact mode of two NM molecules changes from NO_2-to-CH_3 to NO_2-to-NO_2. This is similar to the case of twins in explosives: the head-to-head contact mode of interfacial molecules, dislike the head-to-tail mode in perfect crystal. Obviously, the defect increases the intermolecular potential, or the internal stress, and further reduces BDE as mentioned above.

Conclusions

In summary, we understood the stress-induced activation of decomposition of organic explosives by means of a very simple way: taking the simplest explosive NM as a prototype, constraining one or two NM molecules in a shell to represent their condensed phrase against external stress, and considering the cases of tension and compression, sliding and rotational shear, and imperfection. As a result, we found that the decomposition barriers of NM under all conditions of loading stress decrease relative to the balanced NM monomers or dimers. We thought the origin of the stress-induced activation in all cases is attributed to that the stress always increases repulsive intra- or/and inter-molecular potentials, and its release will be partly contributed to the decomposition of explosive molecules and decrease the barrier of the decomposition. Besides, these models can give explanations of that easier decomposition of gaseous explosives relative to condensed ones and the voids in condensed explosives make them more sensitive to external stimuli.

References

1. Politzer P, Murray J (eds) (2003) Energetic materials, part 2, Ch 1, detonation, combustion. Elsevier, Amsterdam
2. Xiao H (ed) (1994) Molecular orbital theory of nitro-compound. Publishing House of Defense Industry, Peking, in Chinese
3. Delpuech A, Cherville J (1976) Proc symp chemical problems connected with the stability of explosives. Molle, Sweden, 31 May-2 June
4. Kamlet MJ, Adolph HG (1979) The relationship of impact sensitivity with structure of organic high explosives. II. Polynitroaromatic explosives. Prop Explos Pyrotech 4:30–34
5. Rice BM, Samir S, Owens FJ (2002) Density functional calculations of bond dissociation energies for NO_2 scission in some nitroaromatic molecules. J Mol Struct (THEOCHEM) 583:69–72
6. Li J (2010) Relationships for the impact sensitivities of energetic C-nitro compounds based on bond dissociation energy. J Phys Chem B 114:2198–2202
7. Zhang C, Shu Y, Huang Y, Zhao X, Dong H (2005) Investigation of correlation between impact sensitivities and nitro group charges in nitro compounds. J Phys Chem B 109:8978–8982
8. Zhang C (2009) Review of the establishment of nitro group charge method and its applications. J Hazard Mater 161:21–28
9. Rice BM, Hare JJ (2002) A quantum mechanical investigation of the relation between impact sensitivity and the charge distribution in energetic molecules. J Phys Chem A 106:1770–1783
10. Murray J, Lane P, Politzer P (1998) Effects of strongly electron-attracting components on molecular surface electrostatic potentials: application to predicting impact sensitivities of energetic molecules. Mol Phys 93:187–194
11. Zeman S (ed) (2003) A study of chemical micromechanism of the organic polynitro compounds initiation. Energetic materials, part 2. Elsevier BV, Amsterdam, 13:25-52
12. Zhang C (2006) Investigation on the correlation between the interaction energies of all substituted groups and the molecular stabilities of nitro compounds. J Phys Chem A 110:14029–14035
13. Liu W, Zybin SV, Dasgupta S, Klapotke TM, Goddard WA (2009) Explanation of the colossal detonation sensitivity of silicon Pentaerythritol tetranitrate (Si-PETN) explosive. J Am Chem Soc 131:7490–7491
14. Sharma JB, Beard C, Chaykovsky M (1991) Correlation of impact sensitivity with electronic levels and structure of molecules. J Phys Chem 95:1209–1213
15. Zhu W, Xiao J, Ji G, Zhao F, Xiao H (2007) First-principles study of the four polymorphs of crystalline octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine. J Phys Chem B 111:12715–12722
16. Reed EJ, Joannopoulos JD, Fried LE (2000) Electronic excitations in shocked nitromethane. Phys Rev B 62:16500–16509
17. Kuklja MM, Rashkeev SN (2007) Shear-strain-induced chemical reactivity of layered molecular crystals. Appl Phys Lett 90:151913–151916
18. Kuklja MM, Rashkeev SN (2007) Shear-strain-induced structural and electronic modifications of the molecular crystal 1,1-diamino-2,2-dinitroethene: slip-plane flow and band gap relaxation. Phys Rev B 75:104111–104121
19. Zhang C (2007) Computational investigation on the desensitizing mechanism of graphite in explosives versus mechanical stimuli: compression and glide. J Phys Chem B 111:6208–6213
20. Zhang C (2007) Investigation of the slide of the single layer of the 1,3,5-triamino-2,4,6- trinitrobenzene crystal: sliding potential and orientation. J Phys Chem B 111:14295–14298
21. Zhang C, Wang X, Huang H (2008) π-stacked interactions in explosive crystals: buffers against external mechanical stimuli. J Am Chem Soc 130:8359–8365
22. Zhang C (2010) Understanding the desensitizing mechanism of olefin in explosives versus external mechanical stimuli. J Phys Chem C 114:5068–5072
23. Manaa MR, Reed EJ, Fried LE, Goldman N, Galli G, Gygi F (2004) Early chemistry in hot and dense nitromethane: molecular dynamics simulations. J Chem Phys 120:10146–10154
24. Nomura K, Kalia RK, Nakano A, Vashishta P, van Duin ACT, Goddard WA (2007) Dynamic transition in the structure of an energetic crystal during chemical reactions at shock front prior to detonation. Phys Rev Lett 90:148303–148307

25. Manaa MR, Reed EJ, Fried LE, Goldman N (2009) Nitrogen-rich heterocycles as reactivity retardants in shocked insensitive explosives. J Am Chem Soc 131:5483–5487

26. Zhang S, Truong TN (2001) Branching ratio and pressure dependent rate constants of multichannel unimolecular decomposition of Gas-phase α-HMX: an *ab initio* dynamics study. J Phys Chem A 105:2427–2434

27. Zeman S, Atalar T, Friedl Z, Ju XH (2009) Accounts of the new aspects of nitromethane initiation reactivity. Centr Europ J Energ Mater 6:119–119

28. Hu WF, He TJ, Chen DM, Liu FC (2002) Theoretical study of the CH_3NO_2 unimolecular decomposition potential energy surface. J Phys Chem A 106:7294–7303

29. Brill TB, James KJ (1993) Kinetics and mechanisms of thermal decomposition of nitroaromatic explosives. Chem Rev 93:2667–2692

30. Zhang C, Wang X, Zhou M (2011) Isomers and isomerization reactions of four nitro derivatives of methane. J Comput Chem 32:1760–1768

31. Delley B (1990) An all-electron numerical method for solving the local density functional for polyatomic molecules. J Chem Phys 92:508–517

32. Delley B (2000) From molecules to solids with the DMol3 approach. J Chem Phys 113:7756–7764

33. Material Studio 5.5 (2010) Acceryls Inc, San Diego

34. Kohno Y, Ueda K, Imamura A (1996) Molecular dynamics simulations of initial decomposition process on the unique N − N bond in nitramines in the crystalline state. J Phys Chem 100:4701–4712

35. Pospíšil M, Vávra P, Concha MC, Murray JS, Politzer P (2011) Sensitivity and the available free space per molecule in the unit cell. J Mol Model 17:2569–2574