What makes an explosion happen?

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Abstract

Energy density and structure stability are of key concerns in designing and synthesizing energetic materials such as CNHC molecular crystals and the emerging \textit{cyclo-\textit{Ns}} complexes for desired explosive functionalities with a mechanism being open for exploration. An extension of the recent progress in solvation [Sun, Unprecedented O:⇌:O compression and H⇌H fragilization in Lewis solutions (perspective). \textit{PCCP} 21, 2234-50 (2019)] suggests that a combination of the intermolecular hydrogen bond (X:H–Y or HB with ‘:' being electron lone pair of X, Y = O or N ) tension and the super-HB (X:⇌:Y) or anti-HB (H⇌H) compression not only stabilizes the structure but stores energy by shortening intramolecular bonds. The X:H constrains and the X:⇌:Y fosters the explosion. The absence of X:H–Y tension results in the spontaneous aquatic explosion of alkali metals and molten alkali halides. The lack of X:⇌:Y compression fosters no explosion of the molten NaCl in liquid NH\textsubscript{3}, or the molten Na\textsubscript{2}CO\textsubscript{3} or H\textsubscript{3}BO\textsubscript{3} contacting water. The findings may serve as reference for fabricating efficient energy materials.

Keywords: Hydrogen bond; intermolecular interaction; energy storage; structure stabilization

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The combination of intermolecular hydrogen bond \((X:H-Y)\) tension and the anti-HB \((H\leftrightarrow H)\) or super-HB \((X:\leftrightarrow:Y)\) compression not only stabilizes the structure but also stores energy by shortening the intramolecular covalent bonds. The \(X:H\) tension constrains and the \(X:\leftrightarrow:Y\) compression fosters explosion.
Explosions can be categorized into two groups – constrained and spontaneous. The traditional CNHO molecular crystals such as TNT and TATB (1) and the emerging cyclo-N₅s complexes stabilized by acidic entrapment (2-5) undergo constrained explosion. One often expects high energy density yet low sensitivity to perturbation such as thermal excitation or shock wave impulse for practical applications. Once ignited, detonation takes place and the carrier erupts energy variously. The manner, velocity, and amount of energy ejection is subject to its initial storage and the stability, which can be controlled by adjusting the relative number of protons and lone pairs carried by molecular motifs (1). Density functional theory computations (6) suggested that the nonlocal van der Waals interactions is dominant to the cohesive energies of the complex anisotropic molecular crystals, and the dispersion force play roles of even more important in stabilizing the structures (7). However, comprehension of the intermolecular interaction and the manner of energy storage for the constrained explosion is still unclear.

Contrastingly, alkali metals (8) and molten alkali halides (9, 10) explode spontaneously when contacting to water – aquatic spontaneous explosion. When reacting with water at room temperature, Na and molten NaCl explode rigorously with production of H₂, NaOH, shock waves and heat that ignites the H₂ (8, 10, 11). In fact, bulk Na solvation proceeded in four stages in a few seconds (10): first, the Na is dissolved gradually and dyes the water into purple; secondly, the Na specimen releases gas; thirdly, the released gas burns; and finally explodes abruptly. The mixture of Na and K could form a liquid NaK alloy at room temperature. The NaK droplet shoots spikes explosively out when it enters the water, 0.2-0.4 ms immediately after the droplet contacting water (8, 9), see photos in Figure 1a. This explosion process is too fast to be attributed to the heat repellant, instead, alkali metal atoms at the surface of a small cluster each lose its valence electron within picoseconds (8). These electrons dissolve in water and react in pairs to form molecular H₂ and OH⁻ hydroxide. Likewise, solvation of or pouring the molten NaCl (Tm = 801 °C) on ice causes massive explosion under the ambient condition. The explosion readily breaks a fish tank containing water and leaves a cave behind the ice as well. Figure 1 show photos captured from the aquatic explosion of NaK droplet in water and the molten NaCl poured in water and on ice (8, 9).

However, replacing the NaK alloy with a drop of molten Al at ~1,000 °C in water, or pouring molten Cu at 1083°C on ice, produces neither spark nor explosion, instead, displaying the Leidenfrost effect (12) and Rayleigh instability (13). The steam separates the liquid Al and water surface on a 0.1 s timescale. The molten Al just melts and spreads on ice. In contrast, solvation of
molten Na₂CO₃ \((T_m = 851 \, ^\circ C)\) and molten H₃BO₃ \((T_m = 171 \, ^\circ C)\) does not foster an explosion though the melting temperatures of the Na₂CO₃ and the H₃BO₃ are different from that of molten NaCl though the reactions also produce Na⁺ and H⁺. Replacing H₂O with liquid NH₃ at −77.8 °C can form less-apparent transient spikes but does not foster an explosion (8).

Unfortunately, it is unclear what discriminates the constrained from the spontaneous aquatic explosions. Questions also arise what stabilizes the molecular crystals and how to store energy into the crystals. What is the reaction dynamics of the aquatic spontaneous explosion in addition to the initiation by the cationic Coulomb fission (8).

Figure 1. Unconstrained aquatic explosion of (a) NaK alloy droplet when contacting water (8), molten NaCl poured into (b) a water-filled fish tank and (c) on ice. Explosions create spikes abruptly and the molten NaCl explosion breaks the fish tank (9) and (b) leaves a cave behind ice (Tencent video, public domain).

Recent progress in water ice (14, 15) and solvation dynamics (16, 17) advanced the hydrogen bond coupled oscillator pair \((O:H–O \text{ or } HB \text{ with ‘:’ being the lone pair of oxygen}),\) the repulsive \(H\leftrightarrow H\) anti-HB and \(O\leftrightarrow O\) super-HB presented in Lewis acid and basic solutions. These entities can be extended to intermolecular interactions for the explosive substance and reaction processes by replacing O with X, Y = N or O. The \(H\leftrightarrow H\) and \(X\leftrightarrow Y\) repulsion compresses their adjacent intramolecular bonds of the molecular motifs. The \(X: H–Y\) bond stretching lengthens the \(X: H\) but shortens the \(H–Y\) bond because of the Coulomb coupling between electron pairs on the adjacent X and Y (18).
One can imagine what will happen to the intramolecular covalent bonds if paired up the intermolecular H↔H or X:↔:Y compression and X:H–Y tension. This combination shortens all the covalent bonds to store energy whose amount depends on the covalent bond contraction. The combination determines the structural stability and the sensitivity to ignition. Once an X:H breaks, the crystal is crashed and the compressed bonds break catastrophically, detonation takes place. The macroscopic energy release is expected to be coordinated along a single event, as one can observe an explosion though it is subject to numerical computations. However, one should be focused more on the structure stability and energy storage before calculating the impact or amount of energy eruption at explosion.

An extension of the recent findings on solvation charge injection of Lewis solutions and the computation on cyclo-N5- leads to formulation of the explosions on the factors dictating the stability and energy storage. Applying the ever-unaware X:H–Y tension and H↔H or X:↔:Y compression to the inter- and intra-molecular cooperative interactions of the following species (Z = alkali metal; Γ = halide) and processes, shown in Table 1, can clarify factors controlling the constrained and unconstrained explosions.

| Table 1  | Criteria for the constrained and unconstrained explosion. |
|----------|-----------------------------------------------------------|
| category | reactant                                                 | Reaction formulae | Z+↔Z+ fission | X:↔:Y/H↔H compression | X:H–Y tension |
|          |                                                           |                  |                |                           |               |
| unconstrained                               | 2Z + nH2O (ambient T)                                     | 2ZOH + heat + (n-2)H2O + H2↑ | ✓               | ✓                          | ×              |
|                                                   |                                                           | [Z⁺↔Z⁺ + 2(H2O:↔:OH⁻)] + heat + (n-4)H2O + H2↑ |                |                           |               |
| constrained                                  | 2ZΓ(molten) + nH2O                                       | 2ZOH + (n-2)H2O + heat + 2HΓ↑ | ✓               | ✓                          | ×              |
|                                                   |                                                           | [Z⁺↔Z⁺ + 2(H2O:↔:OH⁻)] + heat + (n-4)H2O + 2HΓ↑ |                |                           |               |
| constrained                                  | CHNO*                                                    | [n(X:↔:Y) + m(X:H–Y)] + … | ×               | ✓                          | ✓              |
|                                                   | cyclo-N5 complexes*                                      | [p(H↔H) + q(X:H–Y)] + … |                |                           |               |
| non-explosive                                | 2Z + nNH3 (-78 °C)                                       | [Z⁺↔Z⁺ + H2:N:H–NH] + (n-2)NH3 + H2↑ | ✓               | ×                          | ✓              |
Two steps are involved in the aquatic spontaneous explosion. Firstly, H$_2$O dipoles tend to hydrate the Z alkali metals and the molten Z$\Gamma$ salts as well to dissolve them into constituent ions, Z$^+$ and Z$\Gamma^-$; the Z$^+$ replaces a H$^+$ of the H$_2$O to form the basic ZOH and H$_2$ gas for the Z metal, and H$\Gamma$ for the Z$\Gamma$ salt. Second, hydration of the ZOH base proceeds and turns the ZOH into the well-defined Z$^+$ and OH$^-$ hydroxide (16). In basic solvation, each of the OH$^-$ interacts with its neighboring H$_2$O to form an OH$^-$:4H$_2$O motif and turns one O:H–O bond into the highly repulsive O:$\leftrightarrow$:O super-HB. The second process repeats that of base solvation at a higher temperature.

The O:$\leftrightarrow$:O compression is much stronger than the critical pressure 1.35 GPa for liquid water transiting into ice at the ambient temperature (19). The O:$\leftrightarrow$:O compression softens the H–O bond in liquid water from 3200 to a dispersed band of 2000 ± 200 cm$^{-1}$ and the 1.35 GPa dispersed the same band into 2900 ± 100 cm$^{-1}$. One can imagine the power of the O:$\leftrightarrow$:O repulsion in the second step of Z and molten Z$\Gamma$ solvation that shares the same process of the basic ZOH hydration (16). Therefore, solvation of neutral Z metals and the molten Z$\Gamma$ salts creates excessive O:$\leftrightarrow$:O repulsion at the expense of an O:H–O bond between the solute and the solvent. Thus, the production of [Z$^+$:$\leftrightarrow$:Z$^+$ + 2(H$_2$O:$\leftrightarrow$:OH$^-$) + …] in the basic solution reconciles the unconstrained aquatic explosion without presence of the intermolecular O:H–O tension as the constrains.

However, the absence of super-HB compression fosters no Z metal-liquid NH$_3$ explosion. The replacement of a H with a Z transits the NH$_3$ into H + NH$_2$Z and the solvation turns the NH$_2$Z into the Z$^+$ and the (NH$_2$)$_2^-$ having two pairs of lone pairs and two protons. The (NH$_2$)$_2^-$ performs the same as the H$_2$O and then to form a (NH$_2$)$_2$-(4NH$_3$; or 3NH$_3$ + NH$_2$) motif with its four neighbors. Regularly, each NH$_3$ molecule has three protons and one lone pair. The NH$_3$ interacts with its tetrahedrally-coordinated neighbors through two H$\leftrightarrow$H anti-HBs and two N:H–N bonds, which explains why the NH$_3$ has lower melting temperature at ~78 °C. The (NH$_2$)$_2$-4NH$_3$ motif formation up on Z meal solvation turns at least one repulsive H$\leftrightarrow$H into the N:H–N bond, which stabilizes the ammonia, instead. The transition fosters no explosion but stabilizes the solvent. In contrast, water dissolves the molten Z$_2$CO$_3$ salt and H$_3$BO$_3$ acid into the respective 2Z$^+$ + (HCO$_3$)$_2$ and H$^+$ +
(H\textsubscript{3}BO\textsubscript{3})\textsuperscript{−}, being regular cases of complex salt and acid solvation. The ions polarize their neighboring H\textsubscript{2}O molecules to form each a hydration volume without super-HB or anti-HB being formed (17), though the \(Z^+ \leftrightarrow Z^+\) might be presented. The H\textsuperscript{+} forms a H\textsubscript{3}O\textsuperscript{+} that turns one O:H–O bond into the repulsive H\leftrightarrow H, being insufficiently strong to foster a repulsion.

Figure 2 exemplifies molecular motifs for (a) the TNT (2C\textsubscript{7}H\textsubscript{5}N\textsubscript{3}O\textsubscript{6}), (b) the cyclo-N\textsubscript{5}−:4H\textsubscript{3}O\textsuperscript{+}, and (c) the cyclo-N\textsubscript{5}−: (3H\textsubscript{3}O\textsuperscript{+}+2NH\textsubscript{4}+) complexes optimized from intensive quantum calculations (2, 3). The cyclo-N\textsubscript{5}− can only be stabilized in acidic conditions of the excessive (H\textsubscript{3}O)\textsuperscript{+} or (NH\textsubscript{4})\textsuperscript{+} (4, 20-26). For the TNT in Figure 2a, there are 10 H\textsuperscript{+} and \(2 \times (3+2 \times 6) = 30\) lone pairs “:” surrounding the motif. According to the nonbond counting rules (17), protons and lone pairs can interact with their same kinds of its neighboring motifs to form the X:H–Y, X:\leftrightarrow:Y, or H\leftrightarrow H. There will be 20 HBs and 20 super–HBs per TNT motif with its neighbors. The combination of the X:H–Y tension and the X:\leftrightarrow:Y compression stabilizes the crystals and stores energy into the covalent bonds, which ensures the constrained explosion of the TNT and other CNHO energetic crystals, as well.

Figure 2b illustrates the intriguing force diagram for the cyclo-N\textsubscript{5}−:4H\textsubscript{3}O\textsuperscript{+} stabilization (2). The N atom in the cyclo-N\textsubscript{5}− ring undergoes the \(sp^2\) orbital hybridization with each creating one pair of electron lone pair and one unpaired \(\pi\) electron. These electrons form the dual aromatic components of attraction and compression along the ring (2). At a critical concentration of 4H\textsubscript{3}O\textsuperscript{+} surrounding the cyclo-N\textsubscript{5}−, the resultant repulsion of the circumferential H\leftrightarrow H stretches the radial N:H–O bond, which shortens the H–O and lengthens the N:H. The N:H stretching weakens the compressive aromatic component and reduces the inter-lone-pair repulsion along the cyclo-N\textsubscript{5}− ring. The N–N bond then contracts and gains energy. As shown in Figure 2c for the bond relaxation of the cyclo-N\textsubscript{5}−:(3H\textsubscript{3}O\textsuperscript{+} + 2H\textsubscript{4}N\textsuperscript{+}) complex (3), the N–N bond shortens indeed from 1.38 to 1.31-1.32 Å, the N:H nonbond lengthens to 2.10 Å for the N:H–N bond and to values varying from 2.17-2.26 Å for the N:H–O bonds (2, 3) with respect to the O:H nonbond of 1.70 Å at 4 °C.

Therefore, the N:H–O or the N:H–N tension by the resultant circumferential H\leftrightarrow H\textsuperscript{+} repulsion shortens all the H–O/N and the N–N bonds, which not only stabilizes the cyclo-N\textsubscript{5}− complexes but also stores excessive energy to raise the reactant to the energetic metastable state, as illustrated in Figure 3. This configuration clarifies the reason why the acidic entrapment could stabilize the cyclo-N\textsubscript{5}− (20-24) and why the X:H–Y and X:\leftrightarrow:Y or H\leftrightarrow H coexistence is essential to the constrained explosion. The X:H breaking initiates and the X:\leftrightarrow:X fosters the explosion of the cyclo-N\textsubscript{5}−.
complexes. In the \textit{cyclo-}\textit{Ns} complexes, the H$\leftrightarrow$H repulsion plays a part of stabilization but fosters no explosion as the H$\leftrightarrow$H does in the molten H$_3$BO$_3$ acid solvation.

Figure 2 Molecular motifs for (a) the TNT (2C$_7$H$_5$N$_3$O$_6$), (b) the \textit{cyclo-}\textit{Ns}:4H$_3$O$^+$ with the force diagram, and (c) the \textit{cyclo-}\textit{Ns}: (3H$_3$O$^+$ + 2NH$_4^+$) with bond relaxation. For TNT, the black spheres are carbon, small grey spheres are H, red ones are oxygen and the blue ones are N. Each N carries one and N two pairs of lone pairs. At the critical concentration of stabilization, the radial N:H–O tension by the circumferential H$\leftrightarrow$H repulsion not only stabilizes the \textit{cyclo-}\textit{Ns} complexes but also stores excessive bond energy. The configuration shortens all the covalent bonds and lengthens the N:H nonbond, see context for discussion (reprinted with permission from (2, 3))

Figure 3 Energy diagram for the constrained (BA $\neq$ 0) and unconstrained (BA = 0) explosion. X:H–Y tension and X:$\leftrightarrow$:Y or H$\leftrightarrow$H compression stabilizes the crystal structure (BA). Intramolecular bond

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shortening through X:⇔:Y or H⇔H compression and X:H–Y tension stores energy (CA). Tensile X:H breaking initiates and X:⇔:Y fosters detonation to eject energy (AD) whose manner and amount of energy is subject to its initial storage and structure stability.

Figure 3 summarizes the present discussion. The combination of the intermolecular X:H–Y tension and X:⇔:Y or the H⇔H compression not only stabilizes the molecular structure but also stores energy by shortening the intramolecular bonds. The X:H constraints and the X:⇔:Y fosters the exploration. Once the constraint X:H breaks, the system will collapse erupting energy. Short of X:H–Y tension endows the unconstrained explosion of alkali metals and molten alkali halides; absence of the X:⇔:Y compressions fosters no explosion of alkali metal in liquid NH₃. One should be focused more on the stability and energy before calculating the impact of energy eruption. As the source of life, the electron lone pairs and protons and the forms of their interactions are the key to water, ice, aqueous solutions, energetic carrier for explosion, and beyond.

Declaration
No conflicting interest is declared.

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