

The Chemistry Behind Explosives

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For over a dozen years I have been involved in advising and training the Houston Police Department Bomb Squad and Houston Fire Department in the area of explosives and hazardous chemicals. I have attempted to distill some extensive chemical knowledge to a few simple principles that can provide bomb disposal technicians (and fire fighters) with the key knowledge they need without dangerous oversimplification. The goal of this article is to provide both an understanding of how the knowledge of chemistry can assist in decision making when handling hazardous materials, as well as provide a simple reference on key issues to be considered when faced with the unknown.

Explosives and explosions are all about chemistry. Although an explosion can be defined as a sudden increase in volume and release of energy in an extreme manner, explosions in the context of chemical explosives are uncontrolled, uncontained, chemical reactions. This is why explosives are classified as low or high explosives according to the rates of their chemical reaction (decomposition): low explosives burn rapidly (or deflagrate), while high explosives undergo detonations.

To a chemist the Periodic table of elements allows for the prediction of the physical properties (melting point, boiling point, etc) and chemical properties (acidity, flammability, etc) of each of the elements as well as those of their compounds. It is the chemist's handbook for explaining and predicting the relative stability or reactivity of most simple compounds. When compounds are more complex, chemists can predict their reactivity or stability based upon the structure of the compound. It is because of these tools that knowing the structure of triacetone triperoxide (TATP) immediately offers a chemist insight into its properties,

stability (or rather instability), and even its preparation. But what about those whose lives depend on decision making when presented with unknown compounds? Much like the "tell" of an opponent in a game of poker, it is possible to use a few straightforward concepts to gain an advantage. This is especially true in this era of new chemical explosives.

A good starting point is understanding that everything around us is comprised of matter, and matter exists in three physical forms: solid, liquid (melt), and gas (vapor). For convenience it is common to divide matter into pure substances and mixtures. The simplest way to think about the difference is to consider whether the components of the matter can be separated by physical methods, such as distillation or crystallization. For example, salt can be separated from water by the evaporation of the water, leaving behind salt crystals. Thus, brine (salt water) is a "mixture" not a pure substance. In contrast, the hydrogen and oxygen that make up water can only be separated by a chemical reaction. Pure substances are classified as either elements (e.g., hydrogen and oxygen) or compounds (e.g., water, H_2O). Mixtures can also be subdivided into two categories: homogeneous and heterogeneous. A homogeneous mixture is one in which all the components are in the same phase (or state of matter). A heterogeneous mixture by default is generally defined as a mixture with components in more than one state of matter. These distinctions are a little arbitrary because they depend on the scale of observation. For example, a cup of tea is a homogeneous mixture since by observation you cannot see the different components (water, caffeine, etc.) but if ice is added this is now a heterogeneous mixture since the ice is a solid whereas the tea is a liquid. So why is it that an understanding of the states of the four sub-categories of matter is important in considering the chemistry

of explosives?

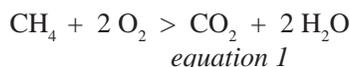
For pure substances whether something is an element or compound can define its hazardous nature. Unless it is radioactive an element in isolation will not be dangerous as an explosive. It will only be its interaction with another element or compound that will trigger the violent chemical reaction we call an explosion. We all appreciate that hydrogen burns, but it only does so in the presence of oxygen (or an oxygen source.) The same may also be true of a compound. For example, octane (one of the constituents of gasoline) also burns only with an oxygen source. However, some compounds have sufficient "oxygen" within their structure or have unstable structures and they can explode without another element or compound being needed.

Even if we have a mixture of the two components for an explosive chemical reaction, the hazards associated with mixtures will depend on whether it is homogeneous or heterogeneous. The rate of a simple combustion reaction depends on how easily the molecules of the two components can get close enough to each other (approximately 10-10 m) to allow for the chemical reaction to occur. Clearly in a heterogeneous mixture the components are only touching at the molecular level where the two phases meet. Thus, only a small fraction of the potential chemical reactions that are possible can occur readily. In a homogeneous mixture each component compound or element is surrounded by its reactive partner. This is essentially the reason why liquid gasoline will simply burn in air when ignited, but gasoline fumes mixed with air will explode.

In considering the combustion (or detonation) of gasoline it should be noted that the hydrocarbon compounds that make up gasoline are quite stable in the ab-

sence of a source of oxygen (usually from the air.) Furthermore, some form of energy input (heat, flame, or spark) must be provided. Thus, the combustion of gasoline provides an archetypal example of the three component explosive systems typical of a traditional chemical explosive: fuel (something that will burn), an oxidizer (source of oxygen), and energy (ignition). While we tend to think of fuel as being organic material there are actually three general classes of fuel: organic (carbon based) compounds, metal, or metal compounds.

Organic compounds generally contain carbon, hydrogen, and other elements (e.g., nitrogen, oxygen.) When an organic compound burns the carbon is converted to carbon dioxide (CO₂) a stable non-flammable compound, while the hydrogen forms water (H₂O) as a vapor (another non flammable compound!) For example, see equation 1.



It is the formation of these two chemicals that is responsible for the energy release we associate with flame or explosion. Thus, essentially any compound of carbon (except carbon dioxide and metal carbonates which can be thought of as salts of carbon dioxide and therefore stable to further oxidation) can act as the fuel in an explosive. So why don't they? As discussed above, the difference between deflagrate and detonation is a function of the rate of reaction, and that in turn, is limited by mass transport i.e., how rapidly the reacting molecules can come together at the molecular level.

Therefore, organic compounds that are dense solids or non-volatile liquids are less likely to be potential fuel sources in explosive. In the absence of other factors (to be discussed below) when

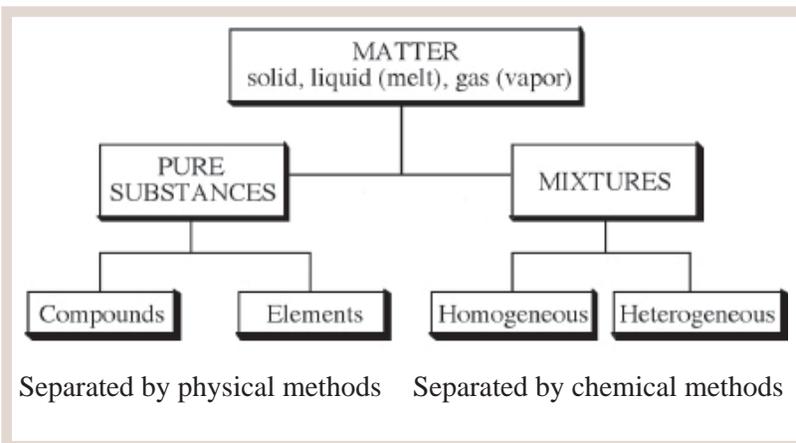


figure 3

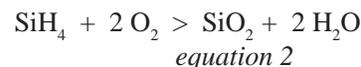
ascertaining if an organic compound is a hazard for explosion the decision should be based on the answers to the following questions: Is there an oxidizer present and if so, how well is it mixed with the fuel (is it homogeneous or heterogeneous?) and; What are possible sources of energy(ignition)?

Despite our reliance on hydrocarbons as a transportation fuel and energy generation, they are not the only things that burn, and hence are not the only potential fuel sources in an explosive mixture. Most metals react with oxygen to form an oxide, but not all of them do it with sufficient energy release for deflagration, let alone detonation. A practical way to predict the reactivity of a metal with oxygen is to look at the stability of the metal oxide: the more reactive a metal, the more stable its oxide. A consideration of rocks, minerals, and salts helps identify some likely candidates. Sapphire and ruby are aluminum oxide, and aluminum is highly flammable with a range of oxygen sources; it is even used as fuel for the space shuttle. Sodium chloride is common rock salt, and sodium reacts explosively with water and burns in air. Magnesium oxide is a mineral that is used as a principal ingredient in construction materials used for fireproofing, while magnesium is highly flammable and can even burn under water and in a carbon dioxide atmosphere.

It is not just reactive metals that can be used as the fuel component of combus-

tion, but also many of their compounds as well. As discussed above, the formation of water from the hydrogen in organic compounds, in combination with an oxygen source, releases significant energy. It stands to reason therefore that any compound comprising of hydrogen and an element can be a potential fuel. A compound

of hydrogen and another element is known as a hydride. This is especially true for the hydrides of reactive metals such as aluminum and sodium, but is also true for the hydrides of silicon and phosphorus. These hydride compounds react with an oxidizer in a manner analogous to that of a hydrocarbon, as may be seen by a comparison of equations 1 and 2.



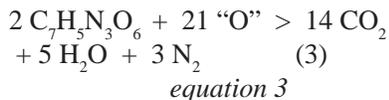
Oxygen (O₂) from the air does not have to be the source of oxidizer. Alternatives such as hydrogen peroxide (H₂O₂), nitrous oxide (N₂O), and nitrates (e.g., ammonium nitrate, [NH₄][NO₃]) are all sources of oxygen for combustion or explosions. Does that mean that every compound containing oxygen can be an oxidizer? The short answer to this is no. For example, alcohols such as methanol will burn (in the presence of additional oxygen), but they will not act as an oxidizer. The oxygen within any compound must be "reactive." By this we mean that it must be able to be released, preferentially as the more reactive oxygen atom (O) rather than O₂ or be attached (chemically bonded to an element that wants to get rid of the oxygen i.e., an element that is readily reduced.) The most likely element in this case is nitrogen, with sulfur and phosphorus also potential candidates. Almost all compounds containing nitrogen bonded to oxygen can act as an oxidizer. Generally, the more oxygen atoms attached to nitrogen the more re-

active the compound.

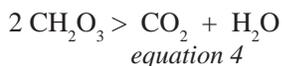
As discussed above, the efficiency of a chemical reaction, such as combustion, is dependent on how well the fuel and oxidizer are mixed at the molecular scale. Obviously the best situation is if both components are in the same molecule. Self-oxidizers are compounds containing oxygen in a reactive form as well as a suitable fuel (carbon or hydrogen.) The most common self-oxidizers are organic nitrates. It should be pointed out that in spite of the presence of reactive oxygen, self-oxidizers may still require an external source of oxygen to ensure complete reaction, and some form of energy input (ignition) is still required.

Given that many compounds contain oxygen, how can we determine whether it will require additional oxidizer to act as an explosive, or whether it has enough to completely self combust, or whether it is itself an oxidizer for other compounds? The simplest test for a compound's potential is its "oxygen

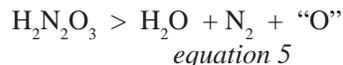
balance." The oxygen balance for a chemical is the amount of oxygen needed or produced to ensure the complete oxidation of all the carbon, hydrogen, or other elements. Compounds such as trinitrotoluene (TNT) have a negative balance since extra oxygen is needed for complete formation of all the CO₂ and H₂O possible. See equation 3.



Despite its reputation as an explosive, TNT is only efficient in the presence of an external oxidant. In contrast, performic acid is an example of a compound with a zero oxygen balance: it has all the oxygen it needs for complete combustion and hence only requires energy to detonate making it a much more dangerous compound per se than TNT! See equation 4.



A positive oxygen balance means that the compound liberates oxygen surplus to its own needs, for example the decomposition of ammonium nitrate provides one atom of oxygen per molecule. See equation 5. Clearly, any compound with a positive oxygen balance makes a good oxidizer and is highly incompatible with combustible chemicals.



Although the majority of chemical explosions involve combustion and therefore require a fuel/oxidizer mixture (even if they are in the same molecule), combustion is not necessary for an explosive. If a molecule is unstable and its decomposition products include gases (such as nitrogen) that result in the sudden increase in volume associated with a detonation, this is called an entropic molecule. Simply put, an entropic molecule is one that generates additional molecules upon decomposition. For example, each molecule of triacetone triperoxide (TATP) generates four mol-

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Applications

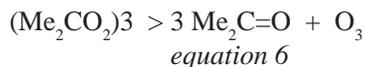
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ecules of product upon decomposition, and since four molecules occupy more space than one, pressure is generated and the gases expand. See equation 6.



Although no combustion is necessary with entropic molecules, their explosive force can be enhanced with additional fuel. The explosive force is a result of a rapid expansion of gases rather than a flame. Both an advantage and disadvantage of entropic molecules is that they often require very low energy input to initiate decomposition and hence detonation. In chemistry, strain in the molecular structure is a good sign of an unstable molecule, but in the case of entropic explosives, looking for the signatures of the gases that will be generated is a much better "tell." In the simplest terms these are the gasses that make up

our atmosphere.

Given its presence as the major component of our atmosphere it is no surprise that N_2 is one of the most stable molecules known. Therefore, any compound that contains more than one nitrogen

forming (N_2) but also two molecules of (H_2) thus producing large volumes of hot gas from a small volume of liquid hydrazine.

Despite its use in combustion (O_2) is also a stable molecule and therefore the presence of compounds containing two oxygen atoms bonded to each other is, like its nitrogen analog, a sign of instability. The most common chemical in this class is hydrogen peroxide (H_2O_2), which liberates oxygen in the presence of sunlight or in the presence of many metals. Organic compounds

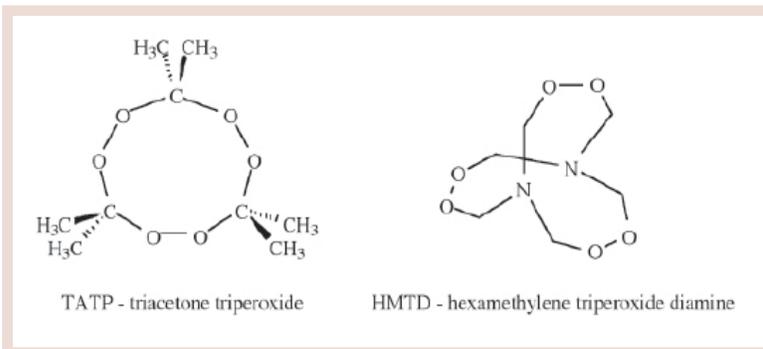


figure 2

molecule, and they are bonded to each other, is clearly a candidate for being an entropic explosive. It is for this reason that most traditional entropic explosives such as lead azide, decompose to liberate nitrogen gas (N_2). Another nitrogen rich compounds is hydrazine (H_2N-NH_2) which again has the potential for

containing the peroxides sub-unit (Figure 2) are much more hazardous, since the oxygen provides both the explosive force and an oxidizer to the remains of the molecule (or other sources of fuel, see above.) Most organic peroxides are made by the reaction of 30% hydrogen peroxide (wood bleach from a hardware

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store) and the base organic (acetone or hexamine fuel tablets) in the presence of an acid catalyst.

The newest generations of entropic explosives are nitramines (Figure 3), which liberate a combination of both N_2 and O_2 doubling their potential effectiveness. The presence of the nitrate group ($-NO_2$) is the key component of a self-oxidizer (see above), while the presence of the N-N bonds provides the instability and entropic energy. Nitramines are prepared from the reaction of amines ($R-NH_2$ or R_2NH where R is an organic group) with nitric acid.

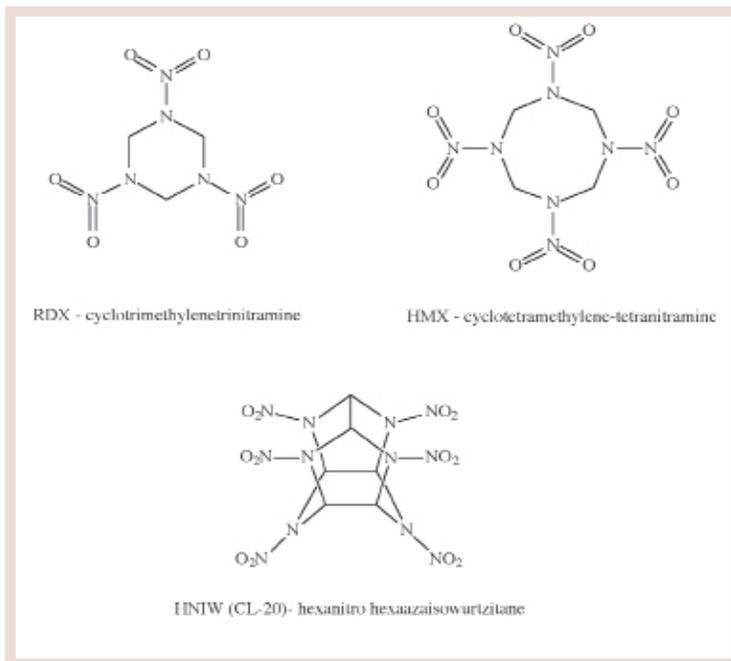


figure 3

In general the higher the N:C ratio of the starting amine the more powerful the resulting nitramine is as an explosive.

This article is not intended to provide a comprehensive understanding of what makes a particular element, chemical, or chemical mixture hazardous. Instead the goal is to provide certain “tells” that will assist in assessing potential hazards. As such this presents some of the key steps for determining if a chemical or chemical mixture not previously encountered poses a threat as an explosive.

Prof. Barron is the Charles W. Duncan, Jr. Welch Chair of Chemistry and a Professor of Materials Science at Rice University. He received his BSc and PhD degrees from Imperial College, London UK and performed post-doctoral research at University of Texas at Austin before spending eight years on the faculty at Harvard University. His research is currently focused on the application of nanotechnology to fundamental problems in energy and health. Research from Prof. Barron's group is the core to three Rice start-up companies. Oxane Materials, NatCore, and Vanguard Solar. After an incident during a lecture at Harvard that resulted in the evacuation of an entire building complex, Barron has been involved in education with the Fire Departments in Cambridge MA and Houston TX. Recently he has helped the Houston Police Department Bomb Squad with training exercises. He has also worked with Harris County District Attorney's office on several criminal cases involving arson.



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