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Experiment #040605-03

"Exhibition chemistry: the detonation of nitrogen triiodide"

Nitrogen iodide (NI_3) was first prepared by B. Courtois in 1813 and was considered to be analogous to nitrogen chloride (NCl_3). NCl_3 was first made by P. L. Dulong in 1811: so obsessed by this simple molecule, he lost an eye and two fingers in its pursuit.

The reaction of iodine with aqueous ammonia yields an explosive brown solid said to be nitrogen triiodide. This simple reaction, however, does not make NI_3 but either [NI_3•NH_3] or [NI_3•$(NH_3)_3$], both are complexes of ammonia. The resulting brown solid, when dry, is extremely shock sensitive, being detonated by the stroke of a feather mounted on a long pole. The result is a loud bang, and an impressive plume of purple-brown iodine vapour. The reaction of iodine crystals with aqueous ammonia can be represented by:

$$3I_2(s) + 5NH_3(aq) \rightarrow NI_3 \bullet NH_3(s) + 3NH_4I(aq)$$

The detonation of NI_3 can be represented by:

$$8NI_3 \bullet NH_3(s) \rightarrow 5N_2(g) + 6NH_4I(s) + 9I_2(s)$$

or simply:

$$2NI_3(s) \rightarrow N_2(g) + 3I_2(s)$$

Components list:
1. 2-3g iodine;
2. 15mL conc.(15M) aqueous ammonia;
3. 50mL beaker;
4. Stirring rod;
5. Spatula;
6. Ring stand and three iron rings;
7. Filter paper;
8. Cellophane tape;
9. 2m pole (feather attached);
10. Ear protection.

The wet nitrogen triiodide ammonia complex is relatively safe to handle. However, if allowed to dry it becomes extremely unstable and even air movement can cause it to detonate unexpectedly. Large amounts must never be made and great care should be taken when handling even modest amounts. Concentrated aqueous ammonia causes burns and is an irritant. Iodine causes burns and the vapour is harmful. The noise from this explosion can leave a ringing in the ears and therefore ear protection must be worn and the audience told to cover their ears.

Procedure:

1. Arrange the three iron rings on the clamp stand ca 15-20cm apart. Put some cellophane tape onto each of the iron rings. This will be used to support the filter paper later.

2. Add 2-3g of iodine to 15mL of concentrated aqueous ammonia in a 50cm3 beaker, stir and let stand for at least five minutes but no longer than 10 minutes. The next part is the most important and must be completed in less than five minutes.

3. Decant the supernatant liquid into a sink and flush with lots of water. Retain the brown solid residue in the beaker and then transfer to a stack of filter papers (ca four) using a spatula. This filter paper absorbs most of the remaining liquid. Divide the wet brown solid into three equal parts and transfer onto three clean filter papers spreading out the solid uniformly. Secure the three filter papers onto the iron rings and place the clamp stand where the audience can see it.

4. You will not be able to move this experimental set up again so think about its location carefully. It is important that it will not be disturbed otherwise it could detonate unexpectedly. It is a good idea to let the brown solid dry for a couple of hours. My experience suggests that the longer you leave it, the better chance you have of a successful detonation. When you are ready to perform the demonstration, touch the bottom filter paper with the feather attached to the pole. The explosion causes the other two portions to detonate.

The detonation will destroy all traces of dry nitrogen triiodide. However, if any does remain, it can be detonated by rubbing with the pole. Otherwise, pour water carefully onto any material containing the brown residue and flush down the sink. Be careful with the stack of filter papers used initially to dry the brown solid. These will contain traces of nitrogen triiodide and should be washed immediately after use.

Here are some simple calculations will you understand that, while NF_3 is thermodynamically stable, the NX_3 (X = Cl, Br, I) are explosive, dangerous materials. By using known data you can show that reaction (a) is exothermic when X = F, but highly endothermic when X = Cl, Br, or I.

$$\tfrac{1}{2}N_2(g) + {}^{3}/_{2}X_2(g) \rightarrow NX_3(g)$$

One may ask why chemical reactions can lead to the formation of very unstable compounds such as NI_3 and $NI_3 \bullet NH_3$. Normally the answer is because endothermic reactions are entropy driven (a negative change in the entropy of the surroundings is offset by a large positive change in the entropy of the system) but this does not appear to be the case here. The answer lies in the fact that very stable compounds are also formed, thus providing the driving force for the reactions. For example, the reaction of iodine crystals with aqueous ammonia is represented by:

$$3I_2(s) + 5NH_3(aq) \rightarrow NI_3 \bullet NH_3(s) + 3NH_4I(aq)$$

Although the enthalpy of formation of $NI_3 \bullet NH^3(s)$ is +146kJ mol-1, the enthalpies of formation of $NH_3(aq)$ (-80kJ mol-1) and $NH_4I(aq)$ (-188kJ mol-1) lead to an enthalpy change for reaction above of -18kJ mol-1, the stability of $NH_4I(aq)$ becomes a critical factor for the reaction to take place.

This demonstration has been adapted from the following source: http://www.rsc.org/lap/educatio/eic/2003/baker_may03.htm