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How Agent Orange Became Toxic: Dioxin Formation - Part 2

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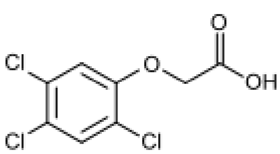
Note: This is Part 2 of a 3-part blog posting. Part 1 discussed the primary components of the Agent Orange herbicide, while here we'll discuss how even more toxic compounds were formed during the manufacture of Agent Orange. The third part will cover the toxicity of dioxins to to humans and other organisms.

Dioxins and furans are are persistent contaminants that can remain in the environment for decades. Typically, dioxins and furans are not created for specific purposes, but are accidental byproducts of the combustion of organic materials at high temperatures. No one ever wants the presence of those toxic compounds during manufacture or release to the environment due to their high health and environmental costs. Here we'll focus on one dioxin that is an highly toxic compound found in certain batches of Agent Orange.

Making chemical compounds is a bit like baking bread. There are many steps which have to be done in the right order, and the bread has to be allowed to rise and then baked at just the right temperature. If any of those steps are missed, or if there is a mistake with the recipe, the bread just won't turn out right.

So let's look at the recipe for 2,3,5-T, and how a simple mistake in temperatures meant that a very toxic dioxin contaminant was introduced to Agent Orange by accident.

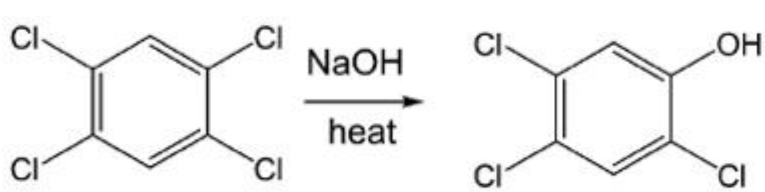
In Part 1, the structure of chlorophenoxyacetic acids formulated for Agent Orange and its 'rainbow' herbicide cousins was outlined. Here is the structure for 2,4,5-T, one of the two compounds in Agent Orange:



2,4,5-trichlorophenoxyacetic acid

Take a look at the forked acetic acid structure connected to the 6-carbon hexagon ring by an oxygen atom. This is an important clue in how dioxins had formed in Agent Orange and other rainbow herbicides.

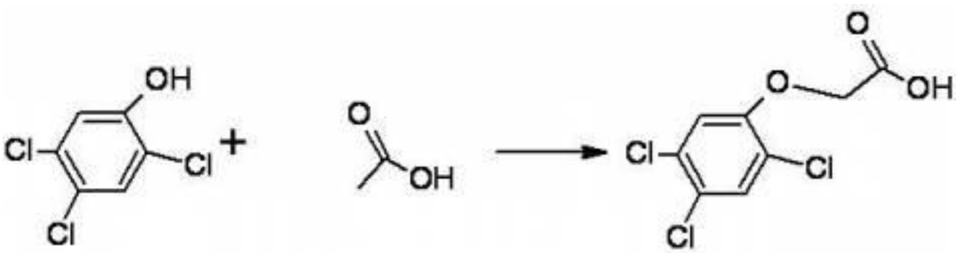
Remember the "O" in the diagram above? The first step in this recipe is to create this "**oxy-**" part of the 2,3,5-T. To do this, two ingredients are needed. Those are benzene (6-carbon hexagon ring) with four chlorides, and the other is sodium hydroxide (NaOH). Increasing the temperature and adding NaOH means that an "OH" molecule is included on the benzene ring. The chemical equation looks like this:



2,3,4,5 benzene + NaOH + heat results in 2,3,5 chlorophenol (From Hites, 2011)

So, after combining the top two ingredients, we now have what is called 2,3,5-chlorophenol.

We need to add the acetic acid fork to the structure to make the 2,3,5-T herbicide. How do we do that? This second step is done by adding chloro-acetic acid to the mixture, which replaces the "H" on the 2,3,5-chlorophenol like this:

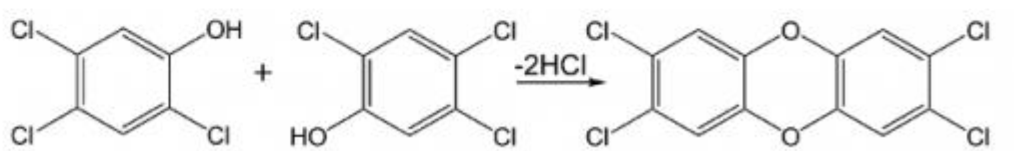


2,3,5-chlorophenol plus acetic acid to form 2,3,5-trichlorooxyacetic acid

The procedure is actually fairly easy. However, maintaining the correct temperature is absolutely vital. Somewhat like baking bread, which has to be done exactly at the right temperature if you don't want to end up with burnt hard pastry or a soggy mess, monitoring the temperature during the first and second steps of making 2,4,5-T is necessary to making sure the reaction happens at the right speed.

The ideal temperature for this reaction is at 180 ºC (356 ºF) and best industrial practices ensure that this temperature is maintained. Unfortunately, if not monitored and adjusted properly, the excess heat from the chemical reactions and other sources will mean that the solution goes above this temperature.

If the temperatures are not monitored and adjusted correctly and exceed 180 ºC, then what happens is that the 2,3,5 chlorophenol molecules become very reactive and start reacting with each other. This creates the toxic compound, "**2,3,7,8-tetrachorodibenzo-p-dioxin**" like this:



2,3,5 chlorophenols reacting together to form 2,3,7,8-TCDD + hydrochloride (From Hites, 2011)

Saying "2,3,7,8-tetrachorodibenzo-p-dioxin" is not easy! It also takes too long to pronounce, so many scientists will just say "dioxins" or to be more specific, "2,3,7,8-TCDD". Like 2,4,5-T, this long chemical name can be broken down to little units, although it takes some effort:

- **2.3.7,8-tetrachloro** = this chemical has 4 chloride molecules attached at specific locations on each of the hexagon rings.
- **dibenzo** = two benzene (hexagon) rings with three double bonds between carbon atoms, with an oxygen molecule attached
- ***p-*** = the type of bond between the benzene rings. It means that there is one oxygen molecule on the opposite side, and the oxygen molecules are not bound to each other.
- **dioxin** = the name of this chemical class.

By a very unfortunate coincidence, 2,3,7,8-TCDD is also one of the *most toxic* human-made substances ever made! Laboratory tests revealed that extremely small amounts would kill mammals.

It is not known how much 2,3,7,8-TCDD was in each batch of Agent Orange produced because at that time, people were only starting to realize the issues.   After measuring concentrations in the environment in Vietnam and other places in North America it is now estimated that approximately 3 parts per million of Agent Orange consisted of this toxic contaminant, which is a very small amount. This is about one drop of water in a bathtub!

So the creation of this dangerous chemical all came down to incorrect temperatures. Yet how can such a small amount of contaminant in a herbicide designed to break down quickly still be considered a serious health risk?

Tomorrow: Toxicity and risk of 2,3,7,8-TCDD and Agent Orange.

References & Resources:

Hites, R. (2011). Dioxins: An Overview and History*. Environmental Science & Technology, 45* (1), 16-20 DOI: 10.1021/es1013664 [Subscription required]

Alvin Young. 2009. Agent Orange and Dioxin Contamination. Chapter 5. *in The History, Use, Disposition and Environmental Fate of Agent Orange*. pages 1-30. [book] DOI: 10.1007/978-0-387-87486-9_5 [Subscription required]

Arseen Seys. *Chapter 9. Dioxins and Furans in the Chemical Industry*. United Nations Environmental Programme Chemicals: Persistent Organic Pollutants. [website] http://www.chem.unep.ch/POPs/POPs_Inc/proceedings/stpetbrg/seys.htm (UNEP POP home page: http://www.chem.unep.ch). (Accessed March 14, 2011) [Free access]

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