Tetra-Amino Macrocyclic Ligand Activators' Affect on Pollution

"Green Chemistry" is emerging as a major field of science in our world today because of the problems we face in the environment. This field of chemistry began in the early 1980s as chemists at Carnegie Mellon University worked to face the problem of pollution. The addition of pollutants, such as estrogen, pharmaceutical products, dyes, and pesticides, into our lakes and rivers has become so common, that it is causing a serious threat to both human and animal health. However, over the last few decades, chemists have created a catalyst known as tetra-amino macrocyclic ligand activators, or TAMLs, to deal with the problem. Even though many are skeptical of the TAML activator, its structure and function result in the success of TAML's use with hormones and dioxins.

<u>The Structure of TAMLs:</u>

Tetra-amino macrocyclic ligand activators are made up of various elements. According to Brown, TAMLs are composed of an iron atom, four nitrogen atoms, water molecules and a carbon ring. Because of the iron base of the molecule, the TAML activator can also be called Fe-TAML. The explanation for how TAMLs are so successful is that these elements are arranged into one synthetic molecule. In addition, the basis of the whole structure is in the center of the molecule, the one iron atom, as seen in Figure 1. Four nitrogen atoms surround the iron atom, strung together by covalent bonds. In these bonds, the atoms share electrons, in contrast to an ionic bond where the electrons are simply taken away. These nitrogen atoms are known as ligands. Connecting the ligands together creates a macrocycle. Within this macrocycle lies the carbon rings. Finally, water molecules are connected throughout, to the ends of the carbon rings (<u>Some Uses</u>).

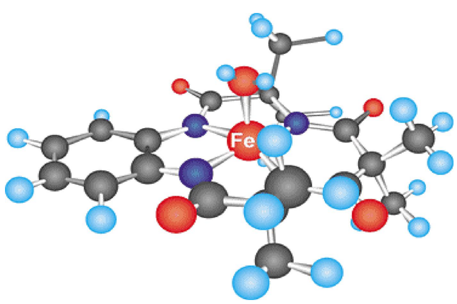

Figure 1: Structure of TAML molecule

What is special about the structure of TAMLs is that these molecules are able to survive the harshest conditions. The most crucial part of the creation of TAMLs was the development of the ligands. The ligands had to be strong enough to endure even the most violent reactions, yet be able to decompose so they wouldn't be a burden on nature afterwards. The ligands of the molecule were to act as a firewall, protecting the iron atom. The creation of the firewall however was not simple. It was a meticulous four step task to find the perfect combination, and was achieved through trial and error. The first step of this process was to create an ideal set of ligands. Once a theoretically ideal firewall was in place, the second phase was to test it with oxidative stresses (Collins 86). Oxidative stress "results from an imbalance between formation and neutralization of pro-oxidants. Various pathologic processes disrupt this balance by increasing the formation of free radicals in proportion to the available antioxidants" ("Oxidative Stresses"). Collins reports that the point of the oxidation stress was to disintegrate the firewall and determine its ability and strength. The third step was to pinpoint the spot of breakdown of the broken down firewall. Finally, the vulnerable atoms were replaced with stronger ones. After years of this process, a perfected firewall was put in place using a combination of nitrogen atoms with carbon rings. However, the creators had to make sure that their ligands were not indestructible because, if they were too strong, the instability of the molecule would make the firewall a determent to the environment.

The Function of TAMLs:

According to Collins, the magic to the abilities of TAML lie in the molecule of hydrogen peroxide, H_2O_2. This molecule enables the reaction to take place, but there are some steps before the hydrogen peroxide can be used with the TAML. To begin, the molecule is dissolved in water. This allows for a water molecule to become a ligand, attaching to the iron based center of the TAML. This state is ready for the entrance of hydrogen peroxide. When the solution is present with hydrogen peroxide it replaces the water molecule ligand attached to the TAML. This results in a molecule of water being expelled. Once the hydrogen peroxide ligand is firmly attached to the TAML, it discards two hydrogen and one oxygen atoms in the form of water. This leaves one oxygen atom attached to the iron atom, but because of oxygen charge of 2-, it tries to take electrons from the iron atom to fill its valence shell. As a result of this interaction, TAML becomes immediately reactive. In this state the TAML is able to break down many molecules that were once thought to be indestructible (87).

TAML activators must be used in very low concentrations; .1 to 4 parts per million in fact (Color Removal). It is needed in such a low concentration because of the potency of TAML. When used properly

TAML is very powerful. According to Sen. Sayam Gupta, even though TAML is used at such a low concentration, it still takes little time for the reaction to fully take place. Over many trials and studies, the synthetic molecule usually completed its task within 6 minutes or less. When tested on phencyclidine, a molecule used in the treatment of wood, TAML effectively destroyed formaldehyde and other toxins, and turned them into biodegradable organic products. The only product to survive the trial was oxalate, a molecule that often results in kidney failure. As research picks up on TAML, this problem is more likely to be fixed.

Ritter confirms that the reaction involving the TAML activator results in biodegradable compounds. He also added that the compounds have a very low toxicity as well. In most of the reactions the toxins were turned to organic acids, dimethyl phosphate, sulfate, nitrite or nitrate. All of these compounds are safe for the environment and will not be a hardship to clean up.

Uses of TAMLs with Hormones:

One of the largest problems linked with pollution is the trouble that hormones, such as estrogen, face with breaking down into less toxic molecules. According to Brown, the problem lies within the mass excretion of 17β-estradiol. This solution is a synthetic version of 17β-ethinylestradiol, and both of these molecules are estrogen based. 17β-estradiol is secreted from cows, whereas 17β-esthinylestradiol is used in birth control. Within the United States, cows and swine produce approximately 10-30 kg of this substance daily along with 20-80 kg of estrone, a major metabolite of estrogen. All three of theses molecules are extremely potent and harmful to the environment. In a study of wastewater in rivers and streams, 17β-estradiol and 17β-ethinylestradiol were found in 10% and 5.7%, respectively, in the waterway observed. 17β-estradiol has a natural half life of around a week, while 17β-esthinylestradiol's half life is about double that.

The result of these molecules being present in the environment has caused a great detriment to both the wildlife and animal population. The molecules can mimic or block various hormones and might disturb the endocrine system. Wildlife could come in contact with the estrogenic compounds through natural waterways, while humans may be faced with contaminated drinking water ("Carnegie Mellon University"). These problems prompted government officials to try to remove these harmful chemicals from the water. When added to TAMLs they are amazingly neutralized in minutes.

Uses of TAMLs with Dioxins:

As a result of the chlorine bleaching of wood pulp in paper mills another deadly molecule is released in the waste water: Dioxins. They are some of the most toxic chemicals that are known to science and pose a serious health threat. Dioxins cause cancer and disrupt cellular growth within animals. Because of the problems faced with the dioxins, TAMLs have been in use in both paper mills and in the treatment of waste, as seen in Figure 2. This eliminates the use of chlorine bleaching which in turns lessens the amount of dioxins released into the environment (Collins, 85).

Figure 2: Demonstration of TAML activators with waste from paper mills. The container on the left is water, the container in the middle is water with waste and the last container on is the waste from a paper mill treated with TAML

Potential Uses of TAMLs:

TAMLs already have several notches in the belt when it comes to helping the environment and the list of future possibilities is endless. According to Ellis, a new strand of TAML is on its way with the hopes of not using halogen substitutes. In theory this will allow for the TAML activator to become better for the environment, because of the lack of a harmful element within the design of the original TAML. McGuiggan also adds that with the experimenting with TAML only beginning, the possibilities for their uses range from cleaning up toxic waste to simply catching loose dyes in a washing machine. Other possible uses of TAML Include being used to rapidly kill biological warfare agents such as anthrax, and will be able to catalyze agents over a wide range of pH, including pHs greater than 14. These ideas are just a glimpse at what TAMLs true potential could be (Some Uses).

Conclusion:

The tetra-amino macrocyclic ligand activator works wonders in an attempt to clear pollution from the environment. The structure and function of the molecule are key to the success of the TAML activator, and the possibility for use this molecule holds is endless. In a world where most environmental news is discouraging, TAML offers a glimpse of what is to come in green chemistry.

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