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ChemMatters (ISSN 0736-4687) is published four times a year (Oct., Dec., Feb., and Apr.) by the American Chemical Society at 1155 16th St., NW, Washington, DC 20036-4800. Periodicals postage paid at Washington, DC, and additional mailing offices. POSTMASTER: Send address changes to ChemMatters Magazine, ACS Office of Society Services, 1155 16th Street, NW, Washington, DC 20036

Subscriber Information

Prices to the U.S., Canada, and Mexico: \$12.00 per subscription. Inquire about bulk, other foreign rates, and back issues at: ACS Office of Society Services, 1155 16th Street, NW, Washington, DC 20036; 800-227-5558 or 202-872-6067 fax.

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Question From the Classroom

By Bob Becker

Q. Our history teacher told us about Benjamin Franklin's experiment of flying a kite in a thunderstorm. What exactly did the experiment involve, what was he trying to show, and why wasn't he killed when the lightning struck?

A. Ah yes, the famous kite-flying investigation! A classic example of an experiment you definitely should **not** try at home, even with adult supervision!

At the time of the experiment (1742), static electricity was a very popular field of research, especially in France and England, Simple experiments showed that two objects charged in the same manner would repel each other, like two glass rods charged by rubbing them with silk or two rubber rods charged by rubbing them with cat's fur. On the other hand, the glass rod was attracted to the silk and the rubber rod to the cat's fur. Some people interpreted this to mean that there were two different types of electricity, which they called vitreous and resinous. If two objects were charged with the same type of Factoid Believe it or not, electricity, they would electricity parties were quite the repel. If charged with difrage among the upper class. ferent types, they would One popular activity at these attract. parties was to use a static-

Franklin argued that charge spark to ignite a cup of there really was but one brandy. Even more popular kind of electricity, and was to charge up a young objects could either be maiden using something like a charged by gaining an hand-cranked van de Graff excess of this electricity generator and then see who or by losing some of it would be daring enough to step and having a deficit. In forward and kiss her! fact, it was Franklin himself who originated the terms "plus" and "minus" as they apply to electricity.

As for the kite experiment, it was designed to test whether the little sparks experienced in their laboratories and the fierce bolts of lightning seen racing across the sky were indeed one and the same. The apparatus was simple. As

Franklin described it, a silk kite with a metal spike protruding from the top was tied to a very long length of twine. This was, in turn, tied to a few meters of silk ribbon. Silk was known to be a nonconductive material, and this ribbon would supposedly give Franklin a "safe" hold of the kite string, but only as long as the silk staved dry on the silk stayed dry, so the experiment also ACS required some sort of shed or shelter to keep him and the ribbon from getting wet. Where the silk and twine were

ioined, a metal key was attached. Once aloft, the spike on the kite was intended to draw some of the "electric fire" out of the sky, and it would travel down the twine and charge up the key. Franklin reported that as he brought his knuckle up to

the key, the same sort of sparking took place as he saw in his lab.

Now to address your final question: why Franklin was not killed? The answer depends on whom you ask. Some historians say that he was just lucky that a fullfledged lightning bolt never actually struck the kite. Only lesser quantities of charge were drawn off (see "stepped leaders" described in the lightning article). Other historians assert that

Franklin knew exactly what he was doing, was fully aware of the potential hazards, and that he had adequately protected himself from any real danger. Sadly enough, some contemporaries who attempted similar experiments. such as the Russian Georg Rikhman,





experiment rather dubious. No one has ever been able to reproduce his results (and survive). Unlike his other experiments, there were no witnesses at the event. The report of the experiment lacks any details or specifics—something very unusual for such a meticulous scientist. In fact, Franklin never did publish a report: He left that to his friend and fellow scientist, Joseph Priestley, 15 years after the experiment reportedly took place!

But why would Franklin invent an experiment that never took place? Tom Tucker believes he knows the answer. In Bolt of Fate (Public Affairs, 2003), Tucker asserts that Franklin was a habitual prankster, perpetuating hoaxes throughout his entire life. Along with all of the inventions he was famous forsuch as the Franklin stove, bifocals, lightning rods, and the glass armonica— Franklin was also a master at inventing stories. He even published dozens of fabricated tales, often using pseudonyms. But why risk his reputation as a scientist by perpetuating such a falsehood? Was it just a prank that got out of control? Not quite. Tucker believes that the hoax was perpetuated intentionally-to get back at a British scientist and scoundrel. William Watson. who took credit for Franklin's pluses and minuses! 👗

Question From the Classroom

What was Benjamin Franklin trying to show with his famous kite experiment? And why wasn't he killed when the lightning struck? Explore the shocking truth about flying kites in nasty weather.

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You bet it can! But some insecticides affect the nerve cells of bugs and humans. Find out why.

Bacteria Power



Chemists Celebr

Stinky mud + water + graphite rod + wire = power?!!! That's right. What's missing is the amazing, naturally occurring bacteria that make it all possible.

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What do you really know about lightning? Find out more about this powerful and deadly phenomenon.

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Can Chemistry Stop What's Bugging You?

By Doris R. Kimbrough

Insect Pests and the Chemicals that Don't Love Them. Sounds like the topic for a tabloid TV talk show, but it's really a battle between adaptable critters and creative chemists.

ou wake up hungry and sneak into your kitchen for a midnight snack. When you flip on the light, two dark and disgusting bugs scurry under the fridge. Ewwww! You grab the



bug spray and drench the area that you can reach, hoping that the insecticide will mean the end of them. You give it one more squirt for good measure and then check the label to see what the lethal agent in the insecticide could be. Chances are the bug spray label reads like a catalog from a chemical company. What is all that stuff? And if it kills bugs, what does it do to humans? Maybe that extra squirt wasn't such a good idea. ... Let's look at the chemistry and find out.

There are several basic groups of chemicals that are used as insecticides. Most of them are "organic", which may seem to be contradictory, but to a chemist, the word "organic" means that the basic framework of the molecule is made of carbon, not that the molecule was grown on a farm without pesticides! Attached to the carbon framework are various other atoms, most typically hydrogen, nitrogen, oxygen, phosphorus, and/or chlorine atoms.

Organochlorine pesticides have chlorine atoms in the structure (go figure!). Examples of Organochlorine pesticides are DDT, aldrin, and chlordane. These have been banned in the United States since the 1970s and 1980s because they persist in the environment and get concentrated as they move up the food chain. Birds and small ani-







Parathion organophosphate insecticide



mals eat insects; bigger birds eat smaller birds and small animals; and the bigger birds (eagles, hawks, falcons) accumulate the pesticide in their fatty tissue. Then when Mama Big Bird lays her eggs, they have extremely fragile shells—so thin in fact that she and Daddy Big Bird would crush them while nesting. Not a nice way to treat your national symbol, so it's a good thing these are banned!

Carbamates have a particular arrangement of carbon, nitrogen, and oxygen atoms. Examples include propoxur, Sevin, and bendiocarb. These were first made and brought into widespread use in the 1950s. Many household pesticides contain carbamates. Pyrethroids can be derived naturally from plants in the marigold/chrysanthemum family or prepared synthetically. Pyrethroids have a characteristic three-membered ring of carbon atoms. These also tend to show up in household sprays.

Organophosphates have a phosphorus atom in the structure; chemists are so good at naming things! Examples include malathion and parathion. These are the heavy-duty pesticides that are more toxic for both the insects and the rest of us. Originally discovered as a result of research into nerve agents for chemical weapons, their use is limited to mostly agriculture rather than households. Both the organophosphates and carbamates work chemically like the nerve gases that are found in some chemical weapons. They are both *acetylcholinesterase inhibitors* (smile when you say that!). This means that they interfere with an enzyme that regulates a neurotransmitter. What does this really mean? Let's look at the chemistry and find out.

Acetylcholine

Acetylcholine is a neurotransmitter, which means that it is one of the many chemicals that make your nerve cells communicate with each other and with the tissues that your nerve cells control, like muscles. Suppose you prick your finger on something sharp. The nerve cells in the place you pricked send an impulse from one end of the cell to the other. As cells go, nerve cells are long; they have extended tentacle-like protrusions that stretch out in a network all along your body. A nerve impulse travels down the nerve cell and gets to the end of the long tentacle. Somehow the impulse has to get from one nerve cell to the next,

so that it can make it all the way to the brain. This is where the neurotransmitter comes in.

Neurotransmitters are chemicals that are released from the end of a transmitting nerve cell to activate the receiving nerve cell. In the brain, there are a large variety of neurotransmitters that all have different jobs and keep your conscious and unconscious systems working. Outside of the brain, the system is simpler because it just has to



communicate with the brain, since the brain does most of the work.

One of the main neurotransmitters in the nervous system is acetylcholine. It is a fairly simple molecule that is synthesized in the nerve cell when choline reacts with acetic acid. It is stored by the cell at the nerve ending. Suppose you touch something sharp.



A sharp prick to your finger triggers an impulse along each nerve cell. Acetylcholine transmits the signal across the gap.

The nerve cells in your finger are activated and send an impulse along each nerve cell. When the impulse reaches the nerve ending, the acetylcholine is released into the space between the nerves, which is called the synapse. It moves across the synapse where it attaches itself to other molecules, called receptors, in the receiving nerve cell. When acetylcholine attaches, a new nerve impulse is triggered in the next cell. This nerve impulse is carried to the next nerve ending, which releases its acetylcholine into the next synapse. The process repeats itself all the way to the brain, which processes the information and sends a message through a similar route back to your finger: "Ouch! Major pain! Pull back! Pull back!" The acetylcholine is also responsible for the interaction between the nerves and the muscles, so the "pull-back" response is controlled by acetylcholine as well.

As you can imagine, this process happens unimaginably quickly, so quickly that you can touch something several times per second and still feel each individual impulse. That's just in case you weren't sure that needle was sharp the first time you touched it! The speed required for this process requires that the acetylcholine gets removed from the synapse very quickly. This is where acetylcholinesterase comes in.

Acetylcholinesterase

Acetylcholinesterase is a huge protein molecule that acts as an enzyme. Enzymes are catalyst molecules that make chemical reactions go faster. The active site of an enzyme is where the chemistry happens. The active site in acetylcholinesterase has an amino acid called serine. The serine has an –OH group that is responsible for the chemistry. Acetylcholine reacts with that serine to make choline, and the acetyl group gets attached to the serine. Then, the choline wanders off to get reabsorbed by the nerve cell (where another enzyme



1. Serine -OH at the active site attacks acetylcholine. Choline is absorbed by the nerve cell.

2. Water reacts with the acetyl-serine group. Acetic acid is produced, and the active enzyme is regenerated.

reattaches the acetyl group to reform acetylcholine). A water molecule reacts with the serine-acetyl group and reforms the serine along with acetic acid. This process happens so fast that a single acetyl-cholinesterase molecule can demolish 10,000 acetylcholines per second! You have this speedy little enzyme to thank for your ability to recognize repeated pokes in the arm from that annoying guy on the bus.

Acetylcholinesterase inhibitors

So what does acetylcholinesterase have to do with pesticides. Well, suppose that you didn't have enough acetylcholinesterase or that it couldn't do its job properly. You would be in a real pickle because the acetylcholine that's sitting unreacted in the synapses of your nerve cells would be making your nerve cells fire and making your muscles react when there was no reason to and you couldn't

control it! One example of this is the involuntary tremors (shaking) you see in people suffering from Parkinson's disease. Another example is your body's reaction to certain pesticides.

Carbamate pesticides are *competitive inhibitors* of the enzyme acetylcholinesterase. This means that they compete with acetylcholine for the enzyme. So the enzyme gets tied up with the pesticide molecule instead of the



Competitive inhibitors temporarily block the enzyme's action.

Irreversible inhibitors attach and never let go!

acetylcholine. Since the carbamate molecules are plugging up the enzyme, they can't work very quickly at breaking down the acetylcholine.

If the acetylcholine builds up in the synapse, it can cause all kinds of physiological reactions such as muscle tremors, excess sweating, difficulty in breathing, coma, and death. Essentially, the nerve becomes excited, but cannot continue to be excited, and so nerve transmission stops. Without nerve transmission, coma and death ensue because the insect can't tell itself to breathe. This is how the carbamates kill the insects and how they can harm you if you are exposed to too much.

Eventually, the body metabolizes the carbamate molecules, and the enzymes can get back to what they are supposed to do:

React with acetylcholine. If you don't die or suffer brain damage while the enzymes are tied up with the carbamates, things get back to normal once the carbamate is used up.

The organophosphate pesticides start out with the same chemistry but wind up with a different ending. They are *irreversible inhibitors* of the enzyme. In this case, they from a stable chemical bond with the enzyme and never let go! Now you are in trouble because the organophosphate has permanently tied up the enzyme, and the acetylcholine molecules are causing your nervous system to go into total overdrive—the actual result is that your muscles contract momentarily as the acetylcholine builds up, then relax as the nerves depolarize and no further impulse can be communicated. This is why organophosphate pesticides are more toxic than carbamates—for insects and for humans.

Pesticides are important and useful molecules. They are important for agriculture and for the control of insect-borne diseases like malaria, West Nile virus, plague, and Lyme disease. We use them to keep bugs from sharing our food, eating our plants, and crawling all over our houses. However, now that you've learned a little bit about the chemistry of some pesticides, you know they should be treated with caution and respect.

Doris R. Kimbrough teaches chemistry at the University of Colorado–Denver. Her article "The Aspirin Effect: Pain Relief and More" appeared in the February 2004 issue of *ChemMatters*.







Building a Better Bleach: A Green Chemistry Challenge

Problem 1: You need to wear your new dark red T-shirt, and there it sits in the dirty clothes hamper. Wait! The washer is loaded and filling with water. Problem solved! You just add the shirt to the rest of the load—the load that happens to be filled with everyone's white shirts, socks, and underwear. You, my friend, are headed for trouble! (See Problem 2.)

Problem 2: You need to find a place to hide when everyone starts screaming about pink underwear and socks!

Problem 3: You need to turn pink back into white.

By Kathryn Parent

stain is a color where you don't want it. It might surprise you that stain removal is actually not *removal* at all. The secret behind getting rid of the unwanted color is not a matter of removing the offending molecules, like detergents acting to remove soil. Instead, the stain molecules are altered chemically so that they no longer reflect light in just the same way as before. We'll call it *decolorizing*, or *bleaching*—words that imply the chemistry going on in the process.

Fine then! Let's get back to the problem at hand. What chemical is going to solve the problem? Let's start with ordinary household bleach. The active ingredient in bleach, sodium hypochlorite (NaOCI), keeps white clothing white and your bathtub sparkling. But handle with care. If you've ever spilled bleach, you know it can also add white blotches to a favorite pair of blue jeans.

How does bleach act on stain molecules? Bleaching is an example of the basic chemical processes—oxidation and reduction—at work. Oxidation is generally defined as *losing* electrons, and reduction as *gaining* them. The two processes occur together, so one compound is reduced in the process of oxidizing another compound. Another common definition of oxidation is the gain of oxygen atoms or the gain of hydrogen atoms. Reduction is then the loss of oxygen atoms or the gain of hydrogen atoms. Here are two ordinary examples.





Back to stains. The color of the stain is a physical property caused by the chemical structure of its molecules. When an oxidizing agent removes electrons from a molecule, the chemical structure of the molecule is changed, and the physical properties (like color) are altered. Chlorine bleaches are oxidizing agents that work efficiently and cheaply in the laundry. Any excess is washed away in the rinse water. Problem solved? Yes, if you're only worried about those pink socks. No, if you're worried about the environment. Sometimes, oxidation with chlorine bleach involves addition of chlorine atoms to the colored stain molecules rather than just removal of electrons. The fact is that the addition of chlorine to an organic-rich waste stream leads to the formation of hazardous byproducts. such as dioxins.

A DIOXIN

hat are dioxins? They're a group of several hundred structurally similar compounds all sharing an uncanny ability to persist and accumulate in the food chain. People exposed to a large amount of dioxins can develop



a condition called chloracne. Not your normal acne, chloracne is a severe skin disease causing lesions to appear on the face and upper body. High dioxin exposure has also been linked to an increased cancer risk in adults. The main sources of dioxins are waste incineration and forest fires. But dioxins can also be produced by industrial processes that use chlorine, like textile and paper manufacturing. Although the exact health risk posed by dioxins is controversial, the tendency for the compounds to linger in the environment prompts the U.S. Environmental Protection Agency to work with industry to find ways to limit their production.

Nonchlorine bleaches to the rescue

If the release of chlorine—especially on a large scale— is bad for the environment, what else can we use to get rid of stains? Alternative "nonchlorine" bleaches are also available. They contain hydrogen peroxide or other peroxide compounds instead of sodium hypochlorite. Because H₂O₂ is a liquid, it is not actually present in solid nonchlorine laundry bleaching products. These solid bleaches contain ingredients like perborate or percarbonate-compounds that react in water to release hydrogen peroxide. Thus, H_2O_2 is the nonchlorine bleaching agent common to almost all of these products. Hydrogen peroxide is also the bleaching agent in many hair dyes. Alone, peroxide alters hair pigments to bestow the "peroxide blonde" effect, but most permanent dyes rely on peroxide as a key ingredient, either to alter natural pigment in the hair or to activate the new dye.

Dilute hydrogen peroxide (3%) is also commonly found in medicine cabinets. Used as an antiseptic for minor cuts and scrapes, it's also effective at removing bloodstains from clothing. The bubbling that occurs when the peroxide encounters blood is due to its decomposition into oxygen gas and water

$H_2O_2 \rightarrow \frac{1}{2}O_2 + H_2O_2$

In the process of decomposing, H_2O_2 releases free radicals—highly reactive inter-

mediates that oxidize other molecules by removing electrons or hydrogen atoms from them. If these other molecules are colored stains or pigments, the chemical changes accompanying their oxidation may alter their physical properties, rendering them colorless—bleached.

Hydrogen peroxide sounds like our ideal bleaching agent! In addition to its everyday use as a household cleaner or hair dye, oxidative bleaching is now used in the pulp and paper, textile, and laundry industries. Hydrogen peroxide (H₂O₂) is a greener, or more environmentally friendly, alternative to chlorine (Cl₂), chlorine dioxide (ClO₂), and sodium hypochlorite (NaOCI) that are traditionally used for bleaching color from substances. And, best of all, hydrogen peroxide does not contain any chlorine atoms. It oxidizes by



ACS STAFF PHOTO



An example of a TAML oxidant activator

either adding oxygen or removing hydrogen atoms. As a result, the oxidized compounds do not include organochlorine-type pollutants, and the problem of hazardous pollution is prevented at the source.

So, what are we waiting for? Why not stop using chlorine bleach altogether and replace it with hydrogen peroxide alternatives? The challenge of replacing traditional chlorine bleaches with hydrogen peroxide is twofold. First, the peroxide oxidation process can be unselective. Because any molecules in the vicinity that are exposed to decomposing hydrogen peroxide get exposed to reactive free radicals, some unwanted chemistry might accompany the desired oxidation. Second, successful bleaching with H₂O₂ requires higher temperatures and pressures and longer reaction time than those required for chlorine bleach. On an industrial scale, this means higher costs for energy, equipment, and labor for the bleaching process.

A research group led by Professor Terry Collins at the Institute for Green Oxidation Chemistry (we'll get to the *Green* part in a minute) at Carnegie Mel-Ion University may have solved our bleaching problems by developing some heroic molecules with names to match. Collectively, they are called *tetraamido macrocyclic ligands* or TAML for short. These versatile molecules (picture above) function as catalysts in the hydrogen peroxide bleaching process. Their presence allows hydrogen peroxide oxidation to proceed at much lower temperatures and pressures. And like all catalysts, they are not consumed in the process.



By using TAML activators, industrial processes like paper making and textile manufacturing that require bleaching, are becoming more energy efficient and less polluting.

That's the kind of good news the Environmental Protection Agency rewards with the annual Presidential Green Chemistry Challenge Awards, a program that recognized Prof. Collins's research team for their innovative research in 1999.

Green chemistry is the design of chemical products and processes that are environmentally benign by design. That means that the products can be made from renewable resources, that they consume minimal energy resources in their manufacture, and that they don't release polluting end-products into the environment that must be cleaned up later. It's easy to see how bleaching with TAML-activated H₂O₂ would be an ideal example of green chemistry in action. Made from naturally occurring biochemicals, TAML catalysts reduce energy costs and not only prevent pollution, but are also useful in cleaning up pollutants that other processes have left behind.

Let's get back to the pink underwear problem. You'll be happy to know that TAML technology has been applied to laundry. Commercial laundries, as well as homeowners in drought-stricken areas are looking for ways to reduce water usage. But using less water leads to problems with dye transfer. The highly selective TAML activators use the peroxide present in some detergents to hunt and destroy free dye molecules, while leaving fabric-bound dye molecules unchanged.

All of which might be too late for your current crisis. But TAML may protect you and your pink-outfitted family from suffering similar laundry mishaps in the future. Check the product labels.

Kathryn Parent is an outreach development consultant for the ACS Green Chemistry Institute.





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More thoughts on bug control

Perhaps, while reading about bug spray and lightning, you happened to consider that not just humans can be electrocuted—bugs can be electrocuted too. In fact, bug zappers are designed to do just that. Are they effective at controlling bugs? Check out http://home.howstuffworks. com/bug-zapper.htm for more information on how bug zappers work.

The Environmental Protection Agency (EPA) has a site—http://www.epa.gov/pesticides/ index.htm—chock full of information about pesticides and suggestions for their safe and effective use. The National Pesticide Information Center also has articles from many sources on pesticides and the implications of their use. http://npic.orst.edu/gen.htm.

Oxford University's chemistry department featured insect repellents in September 2002. They have models and physical properties of DEET and permethrin at

http://www.chem.ox.ac.uk/mom/ insectrepellents/default.htm.

Lightning safety

Do you know the 30–30 rule for lightning safety? According to the National Weather Service, you use the 30–30 rule where visibility is good and there is nothing



obstructing your view of the thunderstorm. When you see lightning, count the time until you hear thunder. A dangerous thunderstorm is within 6 miles if that time is **30 seconds** or less. Seek shelter immediately. Lightning strikes can happen after a storm; wait at least **30 minutes** after the last clap of thunder before leaving shelter. A wealth of lightning and lightning safety information is located at http://www.lightningsafety.noaa.gov/ index.htm.

More on bacteria power

Interested in learning more about Geobacter bacteria? The University of Massachusetts, Amherst maintains a Web site, **http://www.geobacter. org**, with pictures and information on the latest developments. If you decide you want to make your own battery, you might find it invaluable.

Chemists celebrate Earth Day

That's right. The American Chemical Society will observe Earth Day on April 22. The theme for the 2004 Celebration is "What do you know about H₂O?" To heln celebrate

the day, a series of hands-on activities are available for teachers and students at http://chemistry.org/earthday.

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