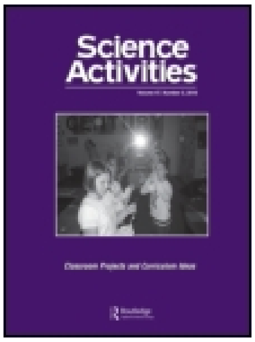

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Illustrating Chemiluminescence with Siloxene Indicator

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Bright orange or yellow light is given off when the substance called siloxene indicator is oxidized. Because the light is intense and the siloxene substance easily prepared, the reaction is suitable for high school and some junior high science classes as a demonstration of chemiluminescence.

The light can be seen easily in a room darkened by closing the drapes or blinds or lowering the window shades. In a very dark room the light is spectacular. The sudden appearance of lighted particles in the swirling liquid is surprising and looks magical.

Siloxene indicator can be prepared by following the steps given below. The teacher should do the preparation, and students may add the oxidizing agent under close supervision. Both students and the teacher should wear safety glasses with solid side shields or goggles when working with any chemical. This rule must be followed in this experiment, since hydrochloric acid is used. One other safety precaution is to follow the procedure exactly without increasing the amounts of the materials.

The chemicals required are concentrated hydrochloric acid, calcium silicide, and an oxidizing agent. Potassium permanganate is the recommended oxidizing agent. Hydrochloric acid and potassium permanganate are available from the usual suppliers of laboratory chemicals, such as Fisher Scientific Company. Calcium silicide can be purchased from Alfa Division, Ventron Corporation, Andover, Massachusetts, at about $35 for 100 grams. This is enough for 500 demonstrations.

Preparation

Step One: Add a 0.20- to 0.30-gram quantity of calcium silicide to 15 milliliters of concentrated hydrochloric acid in a 100 ml. beaker. Stir the reaction mixture gently with a glass rod for about five minutes. The gas which evolves as tiny bubbles is hydrogen. Since hydrogen is flammable, you should keep the beaker in a well-ventilated area, preferably a fume hood, and keep the reaction mixture away from flames and hot objects. After the five-minute stirring period, keep the beaker in the ventilated place for three-and-one-half to five hours.

Step Two: Add water almost to fill the beaker.

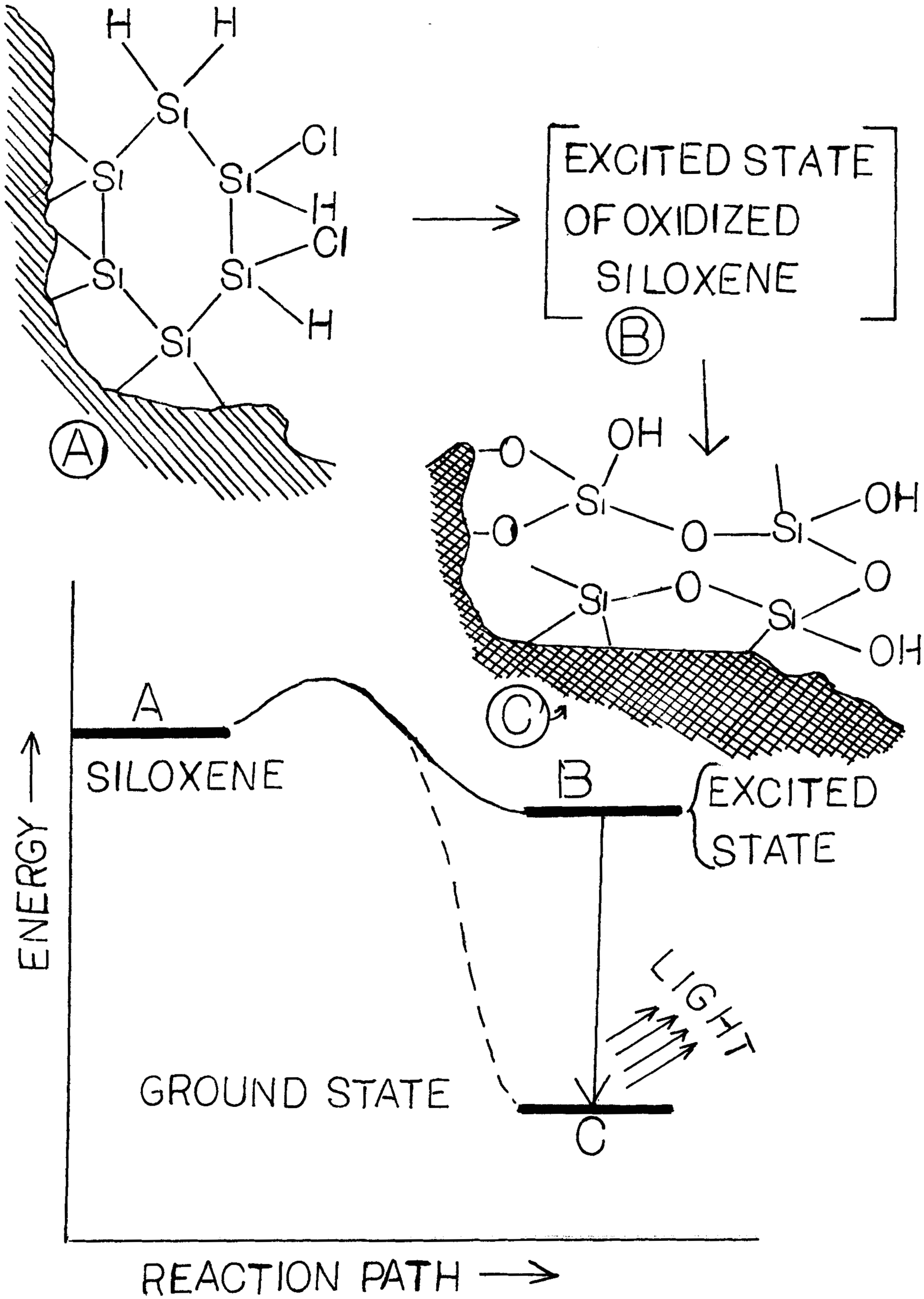
Step Three: Separate the yellow-colored solid from the acid solution by filtration. A Buchner funnel with suction works best, but you can use a normal glass funnel and folded filter paper.

Step Four: Separate the solid from the filter paper and stir it with 100 ml. of fresh water. By filtering again, isolate the solid once more. Repeat this water-washing of the reaction product three times.

Step Five: Separate the siloxene product from the filter paper, and stir it with another 25 ml. of water in a 150-ml. beaker. Heat the beaker on an electric hot plate while stirring until the water boils. Continue the heating for one minute; then remove the beaker from the hot plate and let the product slurry cool to room temperature.

Step Six: Separate the siloxene product by filtration.

Step Seven: Without letting the filtered siloxene product become dry, mix it with 15 ml. of 9 per-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cent hydrochloric acid, which can be made by adding one volume of concentrated hydrochloric acid to three volumes of water. *Remember:* When diluting concentrated acids, *always add acid to water.*

This slurry will retain its light-emitting power for about three days if kept in a small, screw-cap bottle.

The Light-Producing Reaction

Add a small amount of potassium permanganate, amounting to two to three small crystals, to the slurry of siloxene and hydrochloric acid. Shake or swirl the bottle, immediately producing light. It may last from five to thirty minutes, depending on room darkness. When the light fades, you may be able to repeat the reaction by adding another small amount of potassium permanganate.

When the demonstration is completed, you can neutralize the remaining slurry with sodium bicarbonate (baking soda) and wash it down a drain.

If you observe the light-emitting reaction carefully, you will see that the siloxene particles glow. The liquid remains a dark background for the tiny spectacular show of chemiluminescence. To the imaginative, the glowing particles in the dark liquid may look like embers which are sometimes seen at night rising from a campfire. The comparison, however, is only imaginary. The embers of the fire and the siloxene particles radiate visible light for different reasons. Because of their high temperature, embers produce light by a process called incandescence. Almost every substance, if made hot enough, will light up by incandescence. But the glowing siloxene particles are hardly warmer than your hand. Like the bright tail of a firefly, they are hundreds of degrees below the temperature of incandescence.

Siloxene particles produce light directly from the energy of their reaction with the oxidizing agent. Since the conversion is direct, there is no need for heat. The slight heating that the hand can feel on the *outside* of the reaction bottle is due to side reactions.

Of the many thousands of chemical reactions, only a relative few radiate such brilliant light as the oxidation of siloxene. These rare, brilliant reactions follow an unusual pathway through changing energy levels. Scientists often make diagrams to demonstrate such energy changes. A diagram for the energy changes in the siloxene oxidation is given in the lower part of the illustration. The reaction proceeds from level A to level B to level C. Level B, which is called an electronically excited state, is the key to chemiluminescence. Unless its energy path crosses such an excited state, a chemical reaction will remain totally dark. The transition from the excited state to the ground state C produces the light.

The difference in energy between level C and level B controls the color of the light. For light in the visible range the excited state energy above the ground level must be between 40 kilocalories per mol (red) and 70 kilocalories per mol (violet).

In most chemical reactions the excess energy is given up gradually as heat. The energy slides from level A to level C along the dashed line.

As convenient as it is, the energy diagram is only a good way to keep track of energy changes. It tells nothing about what forces the energy of the siloxene oxidation into the excited state.

Siloxene particles are made up of layers of silicon atoms bonded together. A small portion of one layer is illustrated as Structure A. Some of the silicon atoms are also bonded to chlorine atoms and hydrogen atoms. Millions of layers of silicon atoms are stacked to form a small particle. There are strong chemical bonds within each layer but only weak forces holding the layers together.

The oxidizing agent can penetrate between the layers of silicon atoms and oxidize many of them quickly. This reaction leads to the excited state B of unknown structure. The final product is hydrated silicon dioxide, a material similar to common sand. A portion of the structure of the silicon dioxide is shown as Structure C. The cross-hatched area represents the rest of the particle containing trillions of atoms.

In hydrated silicon dioxide the silicon atoms and the oxygen atoms are bonded together in the height, width, and depth of the particles. They are three-dimensional arrays of chemical bonds. Even if you have a very good imagination, it is hard to picture the flat layers of siloxene changing smoothly into such a jungle-gym array of oxygen and silicon atoms. It may be that as the beginning silicon atoms go through contortions because of the oxidation, they become favorably placed for the excited state to form. Is molecular geometry a mysterious factor that forces the siloxene reaction through the excited state? Does geometry compel the reaction to glow with cold but enchanting light? Possibly, but the answers to these intriguing questions are presently unknown. They await some scientist's future discovery.

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