Chemistry

A flash in the crystalline pan

Sometimes it pays to work in the dark. About 17 years ago, chemist Linda M. Sweeting, then a graduate student, was preparing a chemical compound that she had been told was light-sensitive. Working alone and at night, she was astonished to see blue flashes of light as she scraped the freshly crystalized compound off a piece of filter paper into a bottle. Intrigued by her observation, Sweeting explored the subject further and discovered that the phenomenon, known as triboluminescence, was not well understood although it had been studied for centuries. Early reports describe the sparkling light given off when a chunk of crystalline sugar or rock salt is scraped with a knife or crushed in a mortar. Many children have seen similar flashes when rubbing together pieces of hard candy or while watching an open-mouthed companion crunching a wintergreen Life Saver in the dark.

Sweeting, now at Towson State University in Baltimore, has recently come up with an explanation for why one particular compound is triboluminescent. This result suggests a general theory of triboluminescence based on the way electrical charge is separated when crystalline compounds are fractured. Sweeting and Arnold L. Rheingold of the University of Delaware in Newark report their findings in the April 29 JOURNAL OF THE AMERICAN CHEMICAL SOCIETY.

Sweeting and Rheingold studied the compound triethylammonium tetrakis(benzoylmethanato)europate. This particular crystalline substance is known to produce a brilliant orange glow when it is crushed — bright enough to be seen in daylight. By accident, Sweeting discovered that this compound also crystalizes into a second form that is not triboluminescent. By studying the differences between the two crystal structures, Sweeting was able to deduce why one form gives off light and the other does not.

The triboluminescent form, when recrystalized from methanol, appears as irregular, yellow flakes, while the nontriboluminescent form, obtained by recrystalization from the solvent dichloromethane, shows up as yellow tablets. The latter crystals turn out to contain solvent molecules that are trapped within the structure during crystalization. The triboluminescent crystals contain no solvent molecules but show a degree of internal disorder.

Earlier research had indicated that electrical effects play an important role in triboluminescence. As crystals are broken apart, positive and negative charges are separated so that pockets of like charge build up. Then, like miniature lightning bolts, the charges recombine, exciting nitrogen molecules in the air to produce a blue-green glow or causing the chemical compound itself to fluoresce. The problem is determining why the charges are separated in the first place, especially in substances in which molecules are symmetrically arranged.

Sweeting suggests that the disorder found in the fluorescent europate provides the local dissymmetry necessary for charge separation to occur when cracks appear. These crystal imperfections allow small pockets of like charge to accumulate. In nontriboluminescent crystals, the presence of dichloromethane changes the crystal structure just enough to reduce the amount of molecular disorder.

"We believe this discovery of the importance of disorder provides a sufficient condition for the triboluminescence of other centrosymmetric crystals," the researchers conclude, "and that the triboluminescence of other fluorescent materials is excited by light generated by a gas discharge." Sweeting is now studying several other materials to check the theory and plans to investigate the role of impurities in producing triboluminescence. The theory may also apply to the generation of light when rock is fractured (SN: 6/14/86, p.373) and when wet clay dries (SN: 9/12/81, p.166).

Environment

Pesticidal rains

For years, environmentalists have worried about the growing chemical pollution — fertilizers and pesticides — that rainwater washes off of agricultural fields and into lakes and streams. In the May 14 NATURE, researchers at Heidelberg College in Tiffin, Ohio, report identification of a related form of this "nonpoint" chemical pollution — the rainwater itself.

They found 11 pesticides (including herbicides like alachlor, atrazine, butylate and linuron, and insecticides like carbofuran and fonofos) in rains collected at agricultural sampling stations. Though they surveyed rainwater in Indiana and Ohio throughout the spring and summer, they only found the chemicals for about six weeks, beginning right after farmers reported applying them, says R. Peter Richards, an agricultural ecologist at Heidelberg's Water Quality Laboratory. It's because these pesticides break down in a period of weeks to months, he believes, that they are absent in rain the rest of the year.

Ironically, Richards says, "the regulatory agencies didn't think that they needed to worry about the things we studied" — probably because they expected them to break down quickly or to remain bound to soil-sediment particles. In fact the researchers now suspect these chemicals enter the atmosphere through direct evaporation and wind erosion of soil particles onto which the pesticides have been adsorbed.

The levels detected are "orders of magnitude" (one thousand to one million times) lower than levels expected to prove toxic to most non-targeted species. However, the researchers note, "some aquatic algae and simple vascular plants show [adverse] effects at or near these concentrations," and little is known about the possible synergistic effects of exposure to combinations of these chemicals.

Passive smoke: Risk to nonsmokers only?

Numerous reports have shown higher lung-cancer rates among nonsmoking members of a cigarette-smoker's household (SN: 11/22/86, p.325). But a new study of smokers' spouses at the University of New Mexico Medical Center in Albuquerque now suggests that the doubled cancer risk it identified in "passive smokers" — those who breathe in the smoke of others — may be confined only to those who have never smoked. The study, which surveyed the families of 609 lung-cancer cases identified by the New Mexico Tumor Registry and 781 age- and ethnicity-matched controls, showed no increased lung-cancer risk among spouses who had ever smoked themselves — beyond that risk they normally face as current or former smokers. Earlier studies suggest the smokers' risk would still be 10 times higher than that of never-smokers exposed to a spouse's smoking.

Among the study's other principal findings, a never-smoker's lung-cancer risk increased with the duration of exposure to his or her spouse's smoke, but showed no sensitivity to how many cigarettes were smoked per day by that spouse. A report of the work appears in the May AMERICAN JOURNAL OF PUBLIC HEALTH.

Alternatives to ozone-depleting CFCs

Last month the Environmental Protection Agency convened an international panel of experts to explore substitutes for the widely used chlorofluorocarbons known as CFC-11 and -12. These long-lived chemicals, believed to pose a serious risk to stratospheric ozone, are used in refrigeration and in the production of foam insulation. The panel not only identified several more benign alternatives, most notably CFC-134a and -123, but it also found no environmental or technical barriers to their widescale production. The only real obstacle to their substitution, the panel reported, is cost; instead of just 60¢ to 70¢ per pound, the new CFCs would cost between $1.25 and $4 per pound.