Illumination

New & Now

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New & Now

How our brains got bigger, ambulations with animals, reportorial mudslinging, chewy meat substitutes, killer copper, and a chemical reaction revisited.

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Diazonium Ion Hydrolysis
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Novel Reaction

For almost half a century, chemists have assumed that the mechanism through which water replaces nitrogen in diazonium ions was a two-step affair. They were so sure, in fact, that the process has been used to illustrate the basic properties of "unimolecular nucleophilic aromatic substitution" in chemistry textbooks. No longer.

Writing in the Sept. 4 edition of the *Journal of the American Chemical Society*, Rainer Glaser, a professor of chemistry at MU, and doctoral student Zhengyu Wu have demonstrated that the diazonium hydrolysis process -- described by Glaser as the "poster boy of physical organic chemistry" -- is actually accomplished via a single reaction.

"I've thought about it for 20 years and always felt there was something wrong with it," Glaser told journalists recently. "Now it makes sense, and there's not one experiment I cannot explain with this new mechanism. This will be common knowledge for chemists and very influential because we will just know better how the reactions occur."

Diazonium ions are important intermediates in the formation of azo dyes, the artificial yellows, reds and browns found in a variety of processed foods. The implications of Glaser and Wu's discovery, however, go far beyond making hot dogs appear more palatable.

Most important, Glaser says, is how the finding will affect current thinking about DNA connectivity. Of chief interest is nitrosation, the process in which amines, ammonia derivatives, react with nitric oxide or nitrous acid to create diazonium ions within DNA molecules. Because the diazonium ions are not stable, they can react with other materials, causing so-called cross-link formations in DNA's two strands. Such cross-linking inhibits the ability of the strands to unravel and reform during cell division. The malfunction damages cells and could even cause them to become cancerous.

"Our work suggests that there might be other cross-links that have not yet been discovered," says Glaser. "By knowing what happens to DNA, we can learn how it can be damaged. Once you know that, it's the first step in finding how to fix it." Glaser and Wu's research is funded by the National Institutes of Health.

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