Letters

The Photochemical Basis of Cyanotype Photography

In the September 1999 issue of this *Journal*, Lawrence and Fishelson gave a useful summary of the cyanotype process commonly used for printing “blueprints” (*1*). As they report, the fundamental chemistry in the cyanotype process begins when exposure of ferric ammonium citrate to UV light causes the photoreduction of Fe(III) to Fe(II); the citrate counterion furnishes the electrons for the reduction. During their discussion of the chemistry behind the process, they make two observations:

> The chemical reactions taking place in the cyanotype process are not well understood, beginning with the uncertain structure for ferric ammonium citrate.

and later

> Photoactivation results in reduction of Fe(III) to Fe(II), with oxidation of citrate to liberate CO_2, *although the oxidation products have not been identified* [emphasis added].

I am part of a group that has studied the photochemistry of ferric citrate in aqueous solution (*2*) and we can shed some light on the details of the photochemistry involved. The photoreduction of iron is indeed coupled to a photooxidation of coordinated citrate, a process for which we *were* able to identify products. The initial compounds arising from citrate photooxidation are CO_2 and acetone dicarboxylate. That latter compound thermally decarboxylates to form acetone as the ultimate organic product (*2*). The most interesting feature of the system is the pH dependence. At very low pH values, where the Fe and citrate are dissociated or form a 1:1 complex, near-UV light causes no photochemistry. When the pH is raised into the 2–5 range, the photoreaction described above takes place with quantum yields up to 0.45 under the best conditions. We ascribe this pH dependence to the changes in speciation of the system and attribute the photochemistry to dinuclear oxo- or hydroxo-bridged iron citrate species formed by deprotonation of the 1:1 Fe(citrate) complex (*2*).

These solution results allow some inferences to be made about the structure of the photoactive species in the solid-state cyanotype process. The fact that the iron salt used in cyanotype is ferric *ammonium* citrate (rather than 1:1 ferric citrate) is significant. The ammonium ion positive charge compensates for additional deprotonation in the complex beyond the three citrate carboxylate groups. From this I speculate that the photoactive compound in the cyanotype process is a dinuclear complex of the same sort responsible for the solution photochemistry.

Literature Cited

1. Lawrence, G. D.; Fishelson, S. *J. Chem. Educ.* **1999**, *76*, 1199–1200.
2. Abrahamson, H. B.; Rezvani, A. B. ; Brushmiller, J. G. *Inorg. Chim. Acta* **1994**, *226*, 117–127.

Harmon B. Abrahamson
Department of Chemistry
University of North Dakota
Grand Forks, ND 58202-9024
harmon_abrahamson@und.nodak.edu