

The Direct Photolysis of Hexacyanoferrate Complexes: Modeling the Photodissociation Process

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Iron cyanide compounds, in particular the hexacyanoferrate complex, (i.e. $\text{Fe}(\text{CN})_6^{4-}$) are commonly found in surface waters as a byproduct from numerous industrial activities. Hexacyanoferrate is widely viewed as a nontoxic species but following photodissociation (decomposition resulting from sunlight exposure), introduces toxic hydrogen cyanide (HCN, gas and aqueous) into the environment. The ultimate goal of this research is to establish a mathematical model of the photolytic decomposition that $\text{Fe}(\text{CN})_6^{4-}$ undergoes in natural surface waters.

In order to model the photodecomposition of $\text{Fe}(\text{CN})_6^{4-}$, all of the facets of this reaction must be accounted for and understood. The variables that are naturally present must be isolated and analyzed in order to determine what effect, if any, they have on the photolytic process. The list of variables that have been evaluated and the experimental methods used for the replication of these variables are located in Table 1.

In order to simulate the photolysis of the hexacyanoferrate complexes in the laboratory setting, a series of experiments have been conducted. The experimentation began by exposing samples containing a solution of the $\text{Fe}(\text{CN})_6^{4-}$ complexes to UV light at time intervals ranging from 0-35 minutes. The maximum exposure time of 30 to 35 minutes was estimated as sufficient time to allow all of the $\text{Fe}(\text{CN})_6^{4-}$ complexes to decompose and form HCN. The UV light is provided by two different sources: naturally by the sun and artificially by a photoreactor. After the samples have undergone UV exposure, they are analyzed by two separate analytical processes:

- Ion Chromatography – measures the amount of $\text{Fe}(\text{CN})_6^{4-}$ complexes that are present.
- Colorimetry – measures the amount of HCN that has been formed.

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Incorporating these two independent analyses of the CN^- compounds permits the exact relationship between the $\text{Fe}(\text{CN})_6^{4-}$ decomposition and the HCN formation to be mathematically determined.

Results to date indicate that there is a time lag between the disappearance of the hexacyanoferrate complex and the formation of HCN molecules. This could be explained by considering that after the photolytic decomposition has taken place, there are intermediate iron cyanide complexes that exist in the solutions such as $\text{Fe}(\text{CN})_5^{3-}$, $\text{Fe}(\text{CN})_4^{2-}$ etc. that are undetectable with the current testing methods.

Also it would seem logical to assume that turbidity and color would have a similar effect on the photolytic rate since both variables interfere with the UV light transmission through the water sample. However results indicate that the effects of turbidity and natural color differ greatly with the color exhibiting a much more pronounced effect on the rate. The natural color appears to slow the reaction causing the testing time (maximum of 35 minute exposure to the UV source) to be insufficient for the complete transition of the complex cyanide into hydrogen cyanide.

Further testing is underway to establish the exact importance of each variable, to then determine the reaction rates, and finally model the entire process.

Table 1. Characteristics of Surface Waters

Variable	Description / Importance	Experimental Method
Concentration	The amounts of iron cyanide present varies with locations	Changing the concentrations of $\text{Fe}(\text{CN})_6^{4-}$ from 10 ppb – 400 ppb (as CN^-)
Turbidity	The light scattering caused by the colloids present	Addition of Kaolin Clay to the $\text{Fe}(\text{CN})_6^{4-}$ solution
Color	Surface waters are naturally colored by dissolved organic material	Addition of humic acid in concentrations of 5 ppm and 10 ppm to $\text{Fe}(\text{CN})_6^{4-}$ solution
pH	At low pH's the HCN volatilizes and therefore is difficult to quantify with color method	Addition of sodium hydroxide to stabilize the pH at 12 for solutions used in color method
Temperature	Biochemical reaction rates are temperature dependant	Varying the temperature of the solutions in an environmentally significant range.
Light Intensity	Light intensity is a direct determinant of the photolytic rate	Changing the intensity of light in the photoreactor