Swimming Pool Chemistry:
Influence of Cyanuric Acid on OCl^- Photolysis

As mentioned previously "chlorine"- in the form of either OCl^- or HOCl depending on pH- is rapidly lost from pool water upon constant exposure to solar radiation. OCl^- absorbs in the ultraviolet (UV) region of the electromagnetic spectrum and the energy associated with UV radiation is sufficiently strong to break the single bond between the oxygen-chlorine atoms (draw Lewis structure for analysis). A reaction caused by the absorption of sunlight is known as a photolysis reaction (photo = light, lysis = cut...hence "cutting with light"). The following paragraphs are taken from **Chemistry in the Marketplace 4th Edition**, by Ben Selinger, Harcourt Brace & Company, ©1994, pp. 175-191. It's a COOL book!

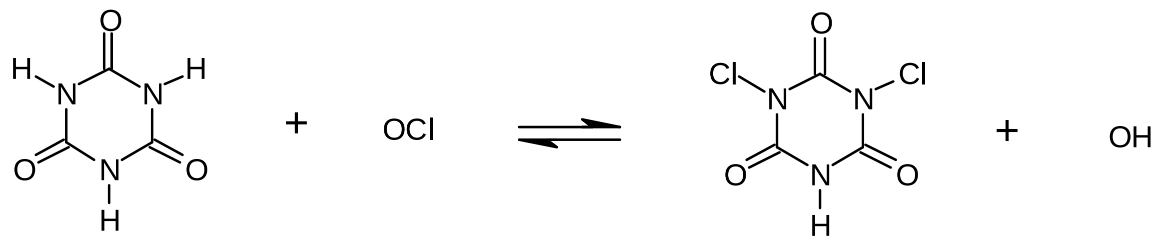
It's estimated that ~90% of hypochlorite lost (consumed) in pools is due to the photolysis reaction below.

$$2OCl^- + h\nu \rightarrow 2Cl^- + O_{2(g)}$$

Where do you think the other ~10% goes? Offer a few suggestions in the space below.

Previously we found out that the photolysis reaction above where λ = 365 nm caused considerable depletion of OCl^- in a short period of exposure time (6 hours for Wednesday and 3 hours for Thursday's labs respectively, hmmm why the disparity?). This comparatively rapid loss of disinfectant capacity begs a question- How is the photolytic depletion of "chlorine" slowed to a respectable rate that doesn't call for constant maintenance? The answer lies in fighting chemistry with chemistry.

Cyanuric acid reacts with OCl^- to give dichloro(iso)cyanuric acid, which is in chemical equilibrium with cyanuric acid and OCl^-. The "iso" is usually left out of the name. See the equilibrium reaction scheme on the next page.



cyanuric acid dichlorocyanuric acid

According to Le Chatelier's Principle, as OCl^- is depleted (a stress applied to the left side of the reaction scheme) via photolysis, the equilibrium shifts from right to left to alleviate the stress, resulting in the depletion of dichlorocyanuric acid and OH^- and the production of cyanuric acid and OCl^-. Consequently, the net depletion rate of OCl^- is slowed because as OCl^- is depleted, it is replenished equally by a shift in the equilibrium above. The $[OCl^-]$ then is maintained at a constant level. This happens as long as the dichlorocyanuric acid has not lost all its chlorine atoms and the pH does not change dramatically for whatever reason.

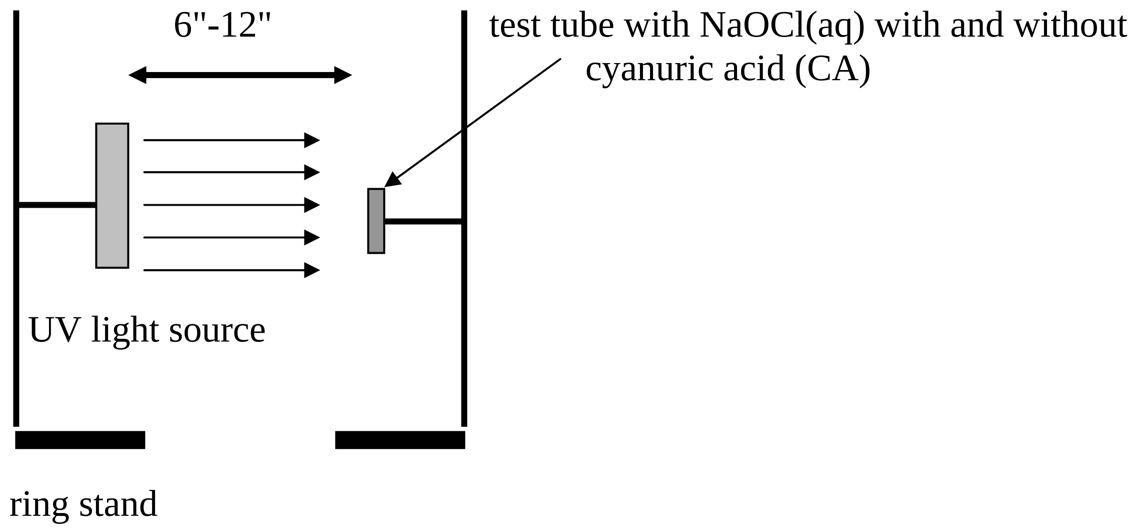
The general commercially available chemicals are trichlorocyanuric acid and sodium dichlorocyanuric acid (typically labeled as sodium dichloro-s-triazinetrione). As expected neither of these compounds are photosensitive; that is neither absorb in the UV region. It would defeat the purpose if they were photosensitive. Draw the structural formulas for each commercial product in the space below.

trichlorocyanuric acid sodium dichlorocyanuric acid

If only cyanuric acid (CA) is added to a pool (and not trichlorocyanuric acid and sodium dichlorocyanuric acid), it's important that the [CA] is properly adjusted. What happens if excess CA is added to a pool? Consider the equilibrium and the effect on [OCl^-]. Provide a brief explanation below.

Procedure:

In this week's lab a simple comparison of the chemistry between a 5ppm OCl^- solution with 2.0mL of 3.09×10^{-2} *M* cyanuric acid (CA) and 5.0mL of 3.09×10^{-2} *M* cyanuric acid, each of which was exposed for three hours to 365 nm longwave UV (see drawing below) and adjusted to the same total volume, will be examined. A comparison of the net change in [OCl^-] over the duration of exposure to UV radiation, Δ[OCl^-], will be made by monitoring absorbance as before with DPD. The change in absorbance is directly proportional to the concentration of OCl^- as shown previously. Based on the chemistry discussed above, which of the two CA solutions would you expect to have a greater Δ[OCl^-]? Why?



Data Table

Both aqueous samples exposed to 365 nm UV radiation for three hours with a distance of 12" between the light source and test tube.

5 ppm OCl^- stock

with 2.0mL CA	5.0mL CA	without CA
A_i =	A_i =	A_i =
A_f =	A_f =	A_f =
ΔA =	ΔA =	ΔA =
$\Delta[OCl^-]$ =	Δ $[OCl^-]$ =	Δ $[OCl^-]$ =