PHOTOOXIDATION OF AMMONIA MECHANISTIC ASPECTS

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The oxidation of NH_3 to HNO_3 is an important industrial process while the oxidation of ammonia fertilizers in soil to nitrites and nitrates has implications in Agriculture. The oxidation of NH_3 in aqueous solutions under UV illumination to yield traces of nitrate has been reported in the older literature. However the mechanism of this interesting conversion has not been investigated.

The oxidation of ammonia was followed by irradiating solutions of NH_4Cl and NaOH with UV light followed by chemical analysis for NH_3, nitrite and nitrate. Changes in $[OH^-]$ were determined by using a sensitive digital pH meter. All kinetic runs were carried out under pseudo-first order conditions with respect to $[OH^-]$ and $[NH_3]$.

It was found that the photooxidation of NH_3 proceeds only under neutral or alkaline pH values and for $\lambda < 254$ nm. Pseudo-first order plots with respect to $[OH^-]$ and $[NH_3]$ indicated that the reaction is first order with respect to $[NH_3]$. The order with respect to $[OH^-]$ was estimated to be Ca. 0.5. An overall rate constant of 3.86×10^{-6} $mol^{-\frac{1}{2}}$ $dm^{3/2}$ s^{-1} has been estimated from the initial rate plots for the above reaction. The oxidation proceeds only to nitrite under normal conditions. With semiconductor suspension where H_2O_2 is generated, the final product is NO_3^-. A free radical mechanism involving an HNO intermediate is proposed for this photooxidation.