

Mechanism of Visible-Light Photooxidative Demethylation of Toluidine Blue O

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Experiments and theoretical calculations by density functional theory (DFT) have been carried out to examine a self-sensitized type I photooxidation of toluidine blue O (TBO⁺). This study attempts to build a connection between visible-light photolysis and demethylation processes of methylamine compounds, such as TBO⁺. We show that controlled photoinduced mono- and double-demethylation of TBO⁺ can be achieved. The kinetics for the appearance rate of the mono-demethylated TBO⁺ and the double-demethylated TBO⁺ were found to fit pseudo-first-order kinetics. DFT calculations have been used to examine the demethylation of TBO⁺ and included N,N-dimethylaniline as a model compound for TBO⁺. The results show an oxygen-dependent demethylation process. The mechanism for the sequential methyl loss is proposed to be due to H[•] or e⁻/H⁺ transfer to 3TBO⁺ followed by a reaction of TBO⁺ with O₂, yielding a C-peroxyTBO⁺ intermediate. Instead of aminyl radical peroxy formation, i.e., N-peroxyTBO⁺, the C-centered peroxyTBO⁺ is favored, that upon dimerization (Russell mechanism) leads to dissociation of formaldehyde from the methylamine site.