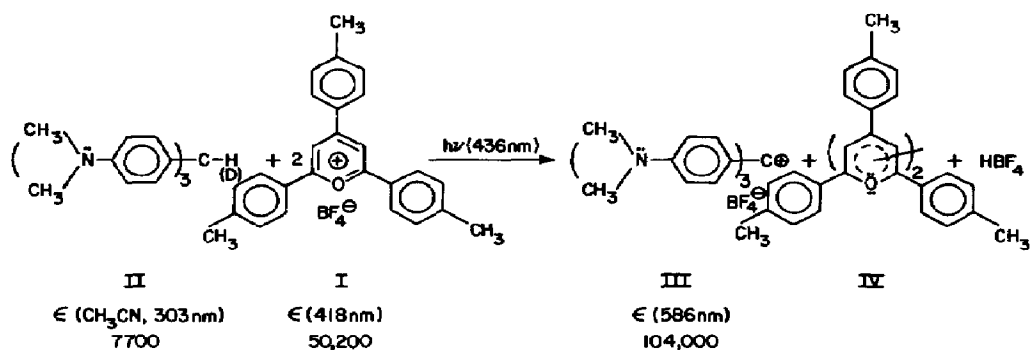


ON THE ELECTRON TRANSFER MECHANISM FOR THE CARBOCATION SENSITIZED PHOTO-  
OXIDATION OF LEUCO CRYSTAL VIOLET

F. D. Saeva and G. R. Olin

Xerox Corporation, Webster Research Center, Webster, New York 14580 (U.S.A.)

The photo-excited carbocation (2,4,6-tri *p*-tolylpyrylium tetrafluoroborate, I) sensitized oxidation of tris(*p*-dimethylaminophenyl) methane (II, leuco crystal violet) to tris(*p*-dimethylaminophenyl) methyl cation (III, crystal violet) occurs by a sequential electron, proton, electron transfer process which is facilitated by molecular oxygen.



The rate of formation of III and the rate of disappearance of I are linear with light intensity and concentration of II in degassed and air-saturated MeCN. Increasing the concentration of I has an inverse effect on the rate,  $d[\text{III}]/dt$ , in degassed MeCN while not affecting this rate in air-saturated solution. In view of the fact that self-quenching of the singlet state of I was not observed over the concentration range studied the inverse rate effect is attributed to the self-quenching of the triplet state.

A reaction scheme for the sensitized photo-oxidation is proposed based on electrochemical redox potentials for

$$\text{I} (E_{1/2}^{\text{red}} = -0.47\text{V} \text{ versus SCE in } \text{CH}_3\text{CN}), \text{II} (E_{1/2}^{\text{OX}} = +0.74\text{V}),$$

$$\text{III} (E_{1/2}^{\text{red}} = -0.80\text{V}), \text{O}_2 (E_{1/2}^{\text{red}} = -0.80\text{V}),$$

product and kinetic information (primary deuterium isotope, i.e.  $k_{\text{H}}/k_{\text{D}} \approx 3.0$ ).