

plex A and the anion of 3,5-DINA. Clustering of H<sub>2</sub>O molecules around the hydrogen-bonded NO<sub>2</sub> group lowers the activation energy required to dissociate E into an anion and an OH· radical. Exciplex A is attacked at C(1) by N and H<sub>2</sub>O, both yielding the complex  $\sigma[C(1)-OH^-]$ . The conversion of A into  $\sigma[C(1)-OH^-]$  by H<sub>2</sub>O requires two steps with a proton abstraction as the second step.

Variations in rate constants caused by the solvent and nucleophile are explained.

### **Photooxidation of aromatic and metalloporphyrin compounds by transition metals to their corresponding radical cation**

GIDEON LEVIN

*College of Environmental Science and Forestry, State University of New York, Syracuse, NY 13210 (U.S.A.)*

The photooxidation of aromatic hydrocarbons and metalloporphyrin compounds to their corresponding radical cations by transition metal salts or organic electron acceptors was studied. For aromatic hydrocarbons such as tetracene and coronene the oxidation of the triplet states is slower than  $10^6 \text{ M}^{-1} \text{ s}^{-1}$ , too slow to be studied by our technique. However, the oxidation of triplet states of zinc tetraphenylporphyrin and magnesium tetraphenylporphyrin by Eu<sup>3+</sup> salts was studied and the corresponding rate constants are  $4.8 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  and  $2.1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ . The oxidation of zinc tetraphenylporphyrin to its radical cation by Fe(ClO<sub>4</sub>)<sub>3</sub> was carried out in carefully purified CH<sub>2</sub>Cl<sub>2</sub>. Flash photolysis of an equilibrium solution of the radical cation, dication and the parent zinc tetraphenylporphyrin compound allows us to study the kinetics of the disproportionation of the radical cation to the corresponding dication.

### **Photolysis mechanism for [Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]K<sub>3</sub> in dimethylformamide**

TATIANA ONCESCU and S.G. IONESCU

*Institute of Chemistry, Department of Physical Chemistry, Bucharest, Bd. Republicii 13, R-70031 (Romania)*

The photolysis of [Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>] K<sub>3</sub> in dimethylformamide at 25 °C in the ligand–metal charge transfer band at  $\lambda = 313 \text{ nm}$  and  $\lambda = 366 \text{ nm}$  was studied. The overall kinetics obeyed a first-order reaction. The rate constants determined allowed us to calculate the reaction quantum yields whose values were