plex A and the anion of 3,5-DINA. Clustering of H_2O molecules around the hydrogen-bonded NO_2 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_2O, both yielding the complex $\sigma[C(1)-OH^-]$. The conversion of A into $\sigma[C(1)-OH^-]$ by H_2O 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

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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 M^{-1} s^{-1}, too slow to be studied by our technique. However, the oxidation of triplet states of zinc tetraphenylporphyrin and magnesium tetraphenylporphyrin by Eu^{3+} salts was studied and the corresponding rate constants are 4.8×10^5 M^{-1} s^{-1} and 2.1×10^6 M^{-1} s^{-1}. The oxidation of zinc tetraphenylporphyrin to its radical cation by $Fe(ClO_4)_3$ was carried out in carefully purified CH_2Cl_2. 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 $[Fe(C_2O_4)_3]K_3$ in dimethylformamide

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The photolysis of $[Fe(C_2O_4)_3]$ K_3 in dimethylformamide at 25 °C in the ligand—metal charge transfer band at $\lambda = 313$ nm and $\lambda = 366$ 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

0.69 ± 0.06 for both the investigated wavelengths. Our quantitative data were explained on the grounds of a reaction mechanism involving an intermediate $[Fe(C_2O_4)_2(C_2O_4 \cdot^-)]^{3-}$ which we detected by flash photolysis. This intermediate decayed by a first-order process with a rate constant $k = (1.46 \pm 0.08) \times 10^3$ s^{-1} according to the structure of a $C_2O_4^-$ monodentate radical coordinated to an Fe(II) oxalate complex.

We also estimated a value of 0.54 for the ratio of the rate constant for the ligand-to-metal charge transfer process to the rate constant for the internal conversion process.

Detection of radical ions in solution: the possible intermediacy of a Rydberg state

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Transient spectra obtained from flash photolysis of benzyl-1-pyrenoate (M) in various solvents with high ionization potentials showed the formation of the triplet state ($\lambda = 425$ nm) and of the radical anion ($\lambda = 510$ nm). The following mechanism is proposed:

$$M \xrightarrow{h\nu} {}^1M^* \xrightarrow{k_{isc}} {}^3M^* \xrightarrow[k_2]{\overset{k_1}{\nearrow} h\nu' \atop +} (M^+ \cdot e^-) \xrightarrow[k_4]{\overset{k_3}{\nearrow} +M} M \cdot^+ + M \cdot^- \xrightarrow[k_6]{k_5}$$

The six rate constants obtained by fitting the transient decays are $k_1 = 1.6 \times 10^2$ s^{-1}, $k_2 = 1.1 \times 10^{10}$ dm^3 mol^{-1} s^{-1}, $k_3 = 2.3 \times 10^3$ s^{-1}, $k_4 = 1.2 \times 10^{10}$ dm^3 mol^{-1} s^{-1}, $k_5 = 1.2 \times 10^{10}$ dm^3 mol^{-1} s^{-1} and $k_6[Q] = 3.5 \times 10^2$ s^{-1}. Their orders of magnitude are those expected from the mechanism proposed which is also consistent with the following experimental data: (a) a lack of correlation with the ionization potentials and efficiency of $M \cdot^-$ formation; (b) the fact that oxygen does not quench the $M \cdot^-$ formation; (c) the dependence of the quantum yield of the $M \cdot^-$ on the square of the light intensity; (d) the fact that the kinetics of formation and disappearance of either transient at 425 and 510 nm excludes an electron transfer process after triplet–triplet annihilation; (e) correlation between the molar polarizability and the quantum yield of the $M \cdot^-$. The hypothesis of a Rydberg state as an intermediate is discussed on the basis of the kinetic evidence and ionization energies involved.