

originates from the *trans* configuration $^3t^*$ of the arylethylenes. The twisted configuration $^3p^*$, which decays into the *trans* and *cis* forms, is in rapid equilibrium with $^3t^*$. The effects of substitution, temperature, solvent and quenchers (azulene and oxygen) on the decay of the $^3t^* \rightleftharpoons ^3p^*$ triplet equilibrium are presented and discussed.

Energy transfer and photochemical changes in molecular crystals

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The rise and decay of the prompt fluorescence from pure and doped anthracene crystals at low temperatures in the 100 ps to 10 ns time range allows the study of excitation energy transfer from the host lattice to guest impurity sites and between different sites occupied by the impurity. For 2-hydroxyanthracene (2-OHA) as the impurity, irradiation of the crystals at elevated temperatures ($T > 200$ K) leads to a photochemical change resulting in heterodimer formation at one of the impurity sites (O_9). A study of the crystals before and after photodimerization allows us to investigate the details of the photochemical change and the roles played by X traps and other structural defects. The experimental arrangement involving a picosecond laser system is briefly described and the results are discussed.

Kinetic and mechanistic aspects of the photoinduced OCH_3 substitution in 3,5-dinitroanisole

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Nucleophiles (N) such as triethylamine and OH^- react with the lowest triplet state of 3,5-dinitroanisole (3,5-DINA) in mixed aqueous solvents, yielding 3,5-dinitrophenolate. In mixed aqueous solvents the primary excited state, prepared by excitation at 353 nm, forms a hydrogen bond prior to intersystem crossing. The hydrogen-bonded triplet state is involved in three parallel reactions with N, producing an exciplex E and two σ complexes with either a C(2)-N or a C(4)-N bond. The latter complexes revert to 3,5-DINA. Bonding in the E involves lone pair electrons on OCH_3 and N. It branches into a more stable exci-

plex A and the anion of 3,5-DINA. Clustering of H₂O molecules around the hydrogen-bonded NO₂ 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 H₂O, both yielding the complex $\sigma[C(1)-OH^-]$. The conversion of A into $\sigma[C(1)-OH^-]$ by H₂O 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 $10^6 \text{ M}^{-1} \text{ s}^{-1}$, too slow to be studied by our technique. However, the oxidation of triplet states of zinc tetraphenylporphyrin and magnesium tetraphenylporphyrin by Eu³⁺ 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(ClO₄)₃ was carried out in carefully purified CH₂Cl₂. 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(C₂O₄)₃]K₃ in dimethylformamide

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The photolysis of [Fe(C₂O₄)₃] K₃ 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