

The perpendicular triplet state of ethylenic compounds observed by nanosecond laser flash photolysis

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Transient absorption assigned to the triplet state in which the double bond is twisted by 90° (perpendicular triplet) was observed by laser flash photolysis of various ethylenic compounds such as α,β -enones (methyl vinyl ketone, cycloheptenone, acetyl cyclohexene etc.) and styrenic derivatives (1-phenylcycloheptene, 1-phenylcyclohexene, substituted styrenes including stilbene and styrene itself). The lifetimes of the perpendicular triplet of these compounds range from 5 to 70 ns depending on the flexibility of the molecular structure and on the nature of the substituents attached to the double bond. The rate constant for quenching of the perpendicular triplets by oxygen is about $(8 - 9) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (in toluene), *i.e.* about one-third of the diffusion rate constant and three times greater than the rate constant for quenching the usual aromatic triplet states: this is in agreement with the theory relating the quenching rate constant to spin statistic factors [1]. In most experiments the triplet states of styrenic compounds were populated by sensitization but population of the triplet states by direct excitation is also possible with quantum yields from 0.1 to 0.3 for *trans*- β -methylstyrene and styrene and with somewhat lower yields (0.05 - 0.1) for compounds such as 1-phenylcyclohexene or α -methylstyrene. Therefore the widely accepted idea that the yield of intersystem crossing is extremely low for flexible styrenic compounds must be revised.

1 J. Saltiel, *Chem. Phys. Lett.*, 37 (1976) 147.

Fluorescence of organic molecules in tenside solutions around the critical micelle concentration

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Relative quantum yields of the blue fluorescence of acridine were measured in protic and aprotic homogeneous solvents of different polarities and in alkaline aqueous solutions of anionic, cationic and non-ionic surfactants around the critical micelle concentration (CMC) as functions of tenside concentration. Measurable quantum yields were detected only in protic homogeneous solutions and in

micellar solutions. At low surfactant concentrations relative quantum yields were independent of surfactant concentration. At concentrations above the CMC, quantum yields decreased drastically and approached constant values between 3% and 30% of that in surfactant-free water (depending on the tenside). This effect is due to protection of acridine from the bulk water, which was found to be more efficient for voluminous micelles. The results permit conclusions to be made on water penetration into micelles and on the solubilization of acridine molecules in micellar solutions.

Thermal and photochemical stabilization of styrene-butadiene polymers

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Synthetic polymers based on styrene-butadiene are widely used in a range of industrial applications. Such polymers are very susceptible to oxidation during production and storage, which leads to considerable polymer cross-linking and loss of physical properties. Analytical studies showed that the oxidative processes involve the unsaturated structural units of the butadiene component and that the autocatalytic thermal and photochemical oxidative mechanisms are basically identical. These involve the initial formation of unsaturated hydroperoxides in the polymer which are thermally and photochemically unstable, producing reactive alkoxy radicals which lead to polymer cross-linking by reactions involving peroxy groups and unsaturated aldehydes and ketones. Polymer cross-linking due to the thermal and/or photochemical attack can be prevented by addition of polymer stabilizers based on alkylaryl-*p*-phenylenediamines which are superior to traditional stabilizers based on phosphites, phenols or polymerized methyl quinolines.

Excitation-energy-dependent rate of internal conversion in cyanine and triphenylmethane dyes

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The radiationless relaxation from the first excited singlet state S_1 to the ground state S_0 is known to be very fast in cyanine and triphenylmethane dyes. The mechanism behind the fast relaxation in these compounds is believed to be