

tween dye triplets and halogen anilines is reported. The magnetic field effect on the yield of free radicals in these systems represents the first direct experimental evidence for sublevel-selective depopulation of triplet states in fluid solution at room temperature.

The mechanism described may induce magnetic field effects on any triplet reaction competing with sublevel-selective deactivation and can thus provide the basis of a general method to study the dynamics of short-lived triplet intermediates.

Kinetics of triplet sublevel selective photochemical reactions in the solid state

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A detailed description of the overall kinetics of photochemical reactions must deal with photophysical activation and deactivation rates as well as with true photochemical rates. On the basis of the hypothesis that the chemical reaction rates of the individual triplet zero field levels have different values for photoreactions involving the lowest excited triplet state, a method is presented for the evaluation of these rates from bulk measurements under steady state illumination conditions. The complications arising from the detection of solid state reactions are discussed, and a simple solution is given, illustrated by a numerical example.

Observation of triplet states of stilbene and related compounds in solution and analysis of the decay mechanism

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Transients formed by energy transfer from triplet donors to stilbenes and arylethylenes are observed in the 360 - 400 nm region by nanosecond laser pulse excitation. The transients (lifetimes in the 100 ns range) are assigned to the lowest triplet state of the arylethylenes rather than to 1,4-biradicals or exciplexes. From spectroscopic and kinetic results, including those from rigid model compounds of stilbene as a comparison, it is suggested that the triplet absorption

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-