A study of the photochemistry of 2-pentanone in solution

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The photochemistry of 2-pentanone was investigated in isooctane and acetonitrile. Type I and type II product quantum yields were found to increase with increasing solvent polarity. The cause of this dependence was investigated by determining singlet and triplet lifetimes at different ketone concentrations. Lifetimes were obtained from sensitized biacetyl luminescence measurements. Kinetic data were derived for intermolecular reactions of the triplet ketone (K) with tributyl stannane (TBS) and *n*-butyraldehyde (BA). Overall quenching efficiencies were found to be high and similar for TBS and BA. However, hydrogen abstraction was predominant in the K–TBS system, while triplet energy transfer prevailed in the K–BA system. The ketyl radical, formed in hydrogen abstraction by the triplet ketone from 2-propanol, was studied by laser flash photolysis. The radical decayed by second-order kinetics. The extinction coefficient for the ketyl radical was estimated from the slope of the second-order plot.

Non-adiabatic outer sphere electron transfer quenching of excited states by Eu(III)

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The original Marcus theory for outer sphere electron transfer reactions is based on the assumption that these reactions are adiabatic. Evidence of non-adiabatic behaviour has recently been discussed for electron transfer reactions involving f electrons of europium ions. We studied the electron transfer reactions between excited states of aromatic molecules and Eu(III) and we analysed the $\log k_q$ *versus* ΔG plots, where k_q is the quenching rate constant and ΔG is the corresponding free-energy change of the reaction. The results indicate that the outer sphere electron transfer reaction is non-adiabatic and that in certain conditions a contribution to the quenching rate constant comes from other more efficient reaction channels involving the formation of a charge transfer intermediate.