

Answer on Question#61076 - Chemistry - Organic Chemistry

Discuss various radiative and non-radiative processes of energy loss from singlet and triplet states of excited molecules.

Answer:

Excited states may be classified as **singlet** or **triplet** based upon their electron spin angular momentum. The electrons in most non-metallic organic compounds are paired (opposite spins) in bonding and non-bonding orbitals, resulting in a net zero spin diamagnetic molecule for the ground state. Such states have a single energy state in an applied magnetic field, and are called singlets. Electronic states in which two electrons with identical spin occupy different orbitals (the Pauli exclusion principle) have a net spin of 1 ($2 \cdot 1/2$) and are paramagnetic. In a magnetic field such states have three energy levels (+1, 0, -1) and are called triplets. Molecular oxygen is a rare example of a triplet ground electronic state. The distinction between singlet and triplet states is important because photon induced excitation always leads to a state of the same multiplicity, i.e. singlet to singlet or triplet to triplet. Since most ground states are singlets, this means that the excited states initially formed by absorption of light must also be singlets. **Internal conversion** of excited states to lower energy states of the same multiplicity takes place rapidly with loss of heat energy (relaxation). Alternatively, an excited state may return to the ground state by emitting a photon (radiative decay). In the study of acetone nearly 80% of the excited singlet states lose energy by internal conversion and about 3% by fluorescence. Conversion of a singlet state to a lower energy triplet state, or vice versa, is termed **intersystem crossing** and is slower than internal conversion. Radiative decay from a triplet state is called phosphorescence and is generally quite slow. The approximate timescales for these transitions are given in the following table.

Process	Transition	Time scale
Light Absorption (Excitation)	$S_0 \rightarrow S_n$	ca. 10^{-15} (instantaneous)
Internal Conversion	$S_n \rightarrow S_1$	10^{-14} to 10^{-11}
Vibrational Relaxation	$S_n^* \rightarrow S_n$	10^{-12} to 10^{-10}
Intersystem Crossing	$S_1 \rightarrow T_1$	10^{-11} to 10^{-6}
Fluorescence	$S_1 \rightarrow S_0$	10^{-9} to 10^{-6}
Phosphorescence	$T_1 \rightarrow S_0$	10^{-3} to 100
Non-Radiative Decay	$S_1 \rightarrow S_0$	10^{-7} to 10^{-5}
	$T_1 \rightarrow S_0$	10^{-3} to 100

The non-radiative decay noted in the last row may take place by intermolecular energy transfer to a different molecule. This collisional process is termed **quenching** if the focus is on the initially excited species, or **sensitization** if the newly created excited state is of interest. Photochemical sensitization commonly occurs by a $T_1 + S_0 \rightarrow S_0 + T_1$ reaction, where the bold red-colored species is the sensitizer. The new triplet excited state may then undergo characteristic reactions of its own.