Photoexcitation And Photoionization Of 7-Hydroxycoumarin And Related Probes

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A combination of furocoumarins (psoralens) and UVA irradiation has been used for over 25 years in a clinical dermatological treatment known as PUVA therapy. Studies have shown that two successive photocycloaddition reactions intercalate the furocoumarin between adjacent DNA base pairs. An understanding of the reactive intermediates that are formed during these photocycloadditions is one of several steps in assessing the long-term safety of the treatment, which is now in question. Coumarins serve as appropriate models for the study of these intermediates, since they are closely related in structure to furocoumarins, but do not form the diadduct described above.

The focus of this study has been the photoexcitation of 7-Hydroxycoumarin (7-HOC) in homogeneous solution, using laser flash photolysis (LFP). Other probes of increased hydrophobicity were also examined using LFP in both homogeneous solution and in phospholipid-bilayer vesicles. This latter case is important since it approaches physiological conditions, which is significant in the context described above.

Previous investigations have shown that substituted coumarins generally give rise to two main signals: those of the triplet excited state (~ 500 nm) and the radical cation (~ 600 nm). In the case of 7-HOC, the positions of the peaks in the transient absorption spectrum were 470 nm and 580 nm, with lifetimes of 400 ns and 4.8 ? s, respectively. Of particular interest is that, unlike other similar coumarins, the higher-wavelength 7-HOC transient was a radical species, rather than a radical cation.

4-Heptadecylumbelliferone (4-HDU) is identical to 7-HOC with the exception of an added heptadecyl tail. This probe was studied in acetonitrile, as well as in phosphate buffer (pH=7.4) containing DMPC vesicles. Using UV-visible, fluorescence, and LFP data, the behaviour of 4-HDU in a quasi-physiological environment will be described. These results will also be related to those obtained for 7-HOC, providing a basis from which the future study of such systems will stem.