Environmental Effects on the Spectra of Photochemically Generated Fluorenyl Radicals

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Summary The electronic spectra of the fluorenyl radicals generated photochemically and trapped at 77 K display a sensitivity to their environment which is almost as large as that of the related carbanions.

ULTRAVIOLET irradiation of the deprotonated form of 9-ethoxycarbonylfluorene leads to the photo-ejection of an electron.[1] We report the effect of the medium on the spectral characteristics at 77 K of photochemically generated 9-ethoxycarbonylfluorenyl and 9-cyanofluorenyl radicals.

For both carbanions, the new absorption between 450 and 580 nm is assigned to radicals formed by electron photo-ejection since: (i) immediately after the beginning of the photolysis, the e.s.r. spectra of the samples prove the presence of trapped electrons; (ii) using neutral filters, it is shown that the rate of disappearance of the anion and the rate of appearance of the radical spectrum are equal and proportional to $I_0^{1.82\pm0.10}$. I_0 is the intensity of the exciting light. This indicates a biphotonic mechanism as observed for electron photo-ejection of various aromatics;[2,3] (iii) the electronic spectrum of the new entity is closely related to that of perchloro-9-phenylfluorenyl radical which is stable at room-temperature;[4] (iv) in the usual ether–isopentane–ethanol mixture (5:5:2 v/v; EPA), the lifetime measured at the wavelength of the new absorption is larger than 24 h.

The electronic transition bands of the radicals are broad compared to the bands of the carbanions or split (0–0 transitions). This can be understood in terms of the two types of environment around the trapped radicals formed in EPA.

The existence of isosbestic points indicates that the ratio of the rates of formation of the radicals in the two environments remains constant during irradiation. A slow thermal transformation is responsible of the modifications of the shape of the first radical absorption bands (555 nm for 9-cyanofluorenyl and 560 nm for 9-ethoxycarbonylfluorenyl radicals). This effect can be reproduced in the dark.

A slight variation of the EPA composition causes a large modification of the ratio of the two components of the split 0–0 bands at 555 and 560 nm. Increase in the proportion of ether leads to an enhancement of the components absorbing at longer wavelengths.

The concentration, nature of cation and anion, the temperature and the solvent all affect the equilibria (1) in which the metal salts of carbanions exist.[5] In ethanol-enriched EPA glass (5:5:3), the sodium salt of 9-ethoxycarbonylfluorene exists primarily as contact ion-pairs.[5,6] The addition of dimethyl sulphoxide (DMSO) shifts the equilibrium to the solvent-separated pair. Irradiation of 9-ethoxycarbonyl sodium in 5:5:3 EPA. gives the spectrum of a radical–metal contact pair showing no sign of broadening or splitting, the addition of DMSO causes a 12 nm shift towards longer wavelengths (solvent separated radical–metal). A similar effect is observed in going from EPA 5:5:3 to EPA 5:2:1.

$$\text{Contact pairs} \rightleftharpoons \text{solvent-separated pairs} \rightleftharpoons \text{free species} \qquad (1)$$

The behaviour of the sodium salt of 9-cyanofluorene necessitates a different interpretation. In 3:4:5 EPA at 77 K, the salt exists essentially as a solvent separated pair[5,6]. As it was observed, the addition of DMSO to this solvent mixture has no effect on the spectrum of the carbanion and its corresponding trapped radical. With 2-methyltetrahydrofuran–1% DMSO as solvent, the equilibrium is considerably shifted towards the free ions. Irradiation of the glassy solution gives a peak at 560 nm, whereas the photolysis in EPA 3:4:5 leads to a first maximum at 545 nm (solvent separated radical–cation species) and a small shoulder on the long wavelength tail of this band corresponding to the species observed in 2-methyltetrahydrofuran–1% DMSO.

Thus the electronic spectra of radicals exhibit a sensitivity to their environment which is almost as large as that of the related carbanions.

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