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Photochemical Reactions of Acetylferrocene

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The early work of Tarr and Wiles [1] on the photochemistry of ferrocenes established that whereas ferrocene itself or alkyl-substituted ferrocenes are quite inert in most solvents except halocarbons, acylferrocenes are much more readily decomposed by light. Consequently, their photochemistry has attracted considerable attention.

From studies of the photolysis of acetylferrocene in alcohols and in the mixtures, methanol-dioxan and water-dioxan, Coyle and Marr [2] postulated electron transfer from an excited state of acetylferrocene to an alcohol (or water) molecule, giving rise to the acetylferricenium ion. It is not clear whether, in view of the moderate stability of the solvated electron in these solvents, it is intended that it be considered as an intermediate in the above process, so that the postulate would parallel that of Traverso *et al.* [3] who proposed electron photoejection for benzoylferrocene.

Previous work [4] showed that when acetylferrocene was illuminated with 254 nm light in ethanol in the presence of N_2O, the yields of N_2 were very small and their dependence on N_2O concentration was consistent with a mechanism involving direct electron transfer to N_2O, which is decidedly a more probable occurrence than electron transfer to ROH. Thus it was thought desirable to investigate more fully the possible processes occurring in hydroxylic media when acetylferrocene is illuminated.

Experimental

Acetylferrocene was prepared from ferrocene by Friedel–Crafts substitution and was purified by column chromatography. All other reagents and solvents used were of AnalaR grade.

The flash photolysis apparatus has been previously described [5]. The quartz cells used were of 15 mm internal diameter by 200 mm light path and had a concentric filter compartment around them. A side-arm and bulb permitted degassing of the solution and saturation with N_2O at a chosen pressure. The techniques for steady illumination were as previously described.

The GLC analysis was performed using a capillary column packed with 10% polyethylene glycol on kieselguhr.

Results and Discussion

When solutions of acetylferrocene (2×10^{-4} mol dm^{-3}) in aqueous borax buffer (pH 9) were irradiated with UV light, significant changes were observed in the electronic spectrum, with the appearance of a large peak at 315 nm. This occurred irrespective of whether the solution was degassed and regardless of whether the exciting light was of wavelength 253.7 nm (from a low pressure mercury lamp) 300–370 nm (from a medium pressure mercury lamp) or 326 nm (from a cadmium lamp, with a filter interposed to remove the 228.8 nm line). In water at natural pH, similar irradiation produced a much broader peak with a maximum at 280 nm. On adding alkali to bring the solution to pH 9, this peak moved to 315 nm and further changes of pH showed that this shift of the absorption was entirely reversible.

When photolyzed buffered aqueous solutions were extracted with CH_2Cl_2, it was found that, whereas the electronic spectrum of the extract was that of acetylferrocene, the spectrum of the yellow aqueous phase had an appreciable peak at about 310 nm, demonstrating that this photolysis product is most probably ionic.

Using as solvent either methanol or ethanol, UV irradiation produced initially only a small change in the electronic spectrum, *viz.* a slight increase in absorption between 275 and 450 nm. Prolonged irradiation led to the build-up of a peak at 285 nm: addition of base caused the peak to move to 315 nm. Further experiments using filter solutions to select the range of incident wavelengths from the medium pressure mercury arc indicated that the observed photo-effects are caused chiefly by light within the 337 nm absorption band of acetylferrocene.

Flash photolysis studies were carried out on degassed solutions (2×10^{-4} mol dm^{-3}) of acetylferrocene in water, in aqueous borax buffer, in ethanol and in methanol. Even when the full spectrum of the photoflash was allowed to reach the sample, no absorption change, transient or permanent, was observed in the wavelength range, 500–750 nm. The minimum detectable absorbance change would be approx. 0.001 for times greater than 100 μs after the commencement of the flash but, because of scattered light from the photoflash, it would be approx. 0.005 at 50 μs after the onset of the flash. However, in view of the long (20 cm) path length and the extinction coefficients of the hydrated electron (18,500 M^{-1} cm^{-1}) and of the ferricenium ion [6] (340 M^{-1} cm^{-1}), it may be seen that maximum possible concentration which may be present within 100 μs of the onset of the flash, either of the solvated electron or of the acetylferricenium ion, is minute. Thus results of these experiments argue strongly against the hypothesis of Coyle and Marr [2].

Analyses of irradiated solutions using 1,10-phenanthroline showed that free Fe^{II} was present in all cases and that the degree of conversion was highest in the aqueous solutions. The presence of cyclopentadiene among the photolysis products in aqueous solutions was demonstrated by extracting with CCl_4 and analyzing by GLC, which showed peaks not found from the extract of an unphotolyzed solution and coincident with those of an authentic sample. This showed that the finding of Ali, Cox and Kemp [7], who detected cyclopentadiene among the photolysis products of benzoylferrocene in moist dimethylsulphoxide, is not peculiar to that solvent. Similar parallels were found when IR spectra were run on solutions of acetylferrocene in methanol, one unirradiated and the other irradiated with stirring with light of 254 nm. The irradiated solution showed new peaks at 1550, 1710 and 1740 cm^{-1}, with minor differences in the range 1000–1100 cm^{-1}.

Our studies in these hydroxylic solvents thus support the view that the basic process leading to rupture of the molecule is not electron photo-ejection or electron transfer to a solvent molecule, but may be internal charge transfer. Although, like Ali, Cox and Kemp [7], we also detect cyclopentadiene and the IR peaks characteristic of a carboxylate group, the product assignment of these authors, a solvated monocyclopentadienyl iron carboxylate, appears to be not entirely correct, since such a moiety would not be expected to exhibit such pH effects in its electronic spectrum.

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