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Preliminary communication

PHOTO-OXIDATION OF 3-FERROCENYLPROPANOATE ION

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Summary

When 3-ferrocenylpropanoate ion is excited by light of around 250 nm, it readily transfers an electron to N_2O and is converted into the anion of 2-carboxyethylferricenium.

Earlier work has shown that electron transfer can occur from photoexcited states of ferrocene and alkyl-substituted ferrocenes to an electron acceptor such as N_2O [1]. The lifetimes of these excited states were deduced to be of at least nanosecond duration. Here we report analogous studies on 3-ferrocenylpropanoic acid, $Fc(CH_2)_2COOH$ (I) (where $Fc \equiv$ ferrocenyl, $C_{10}H_9Fe$), where the carboxylate group permits the use of water as solvent and the methylenes interposed between it and the ferrocene nucleus minimise the electronic interaction between them.

Aqueous solutions of the anion of I at pH 9 were prepared in doubly-distilled water using borax buffer. Irradiation of the deaerated solution with light of 253.7 or 228.8 nm had negligible effect on the electronic spectrum of these solutions. When N_2O was added, illumination with either wavelength caused the solution to turn bluish-green and N_2 was produced. When the unchanged acid was removed by acidifying and extracting with CH_2Cl_2, a stable blue solution was obtained with pronounced absorption bands centred at 255 nm (intense) and 620 nm (weak).

By using the reducing agent $TiCl_3$, this substance was converted into an acid, identified as I on the basis of m.p., TLC and IR. By reason of these reactions and of the similarity of the spectrum to that of the ferricenium ion [2], we propose that (in acid solution) the blue compound is 2-carboxyethylferricenium (II). This compound may also be obtained by chemical oxidation using perchloric acid.

Two possible mechanisms (eq. 1 and 2) may be envisaged for the photo-

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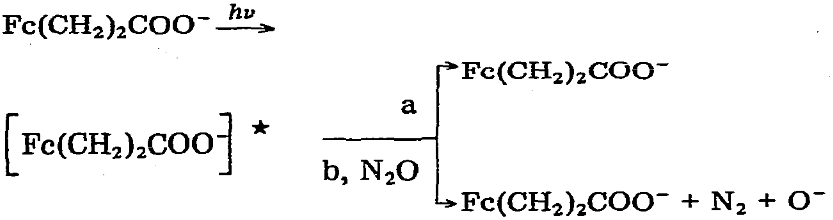
chemical process, viz. (1) photo-ejection of an electron from the anion of I followed by reaction of the (solvated) electron with the electron scavenger, N_2O, and (2) direct electron transfer from a photo-excited state of the anion of I to N_2O.

$$\mathrm{Fc(CH_2)_2COO^-} \xrightarrow{h\nu} \mathrm{\overset{+}{Fc}(CH_2)_2COO^-} + e^-_{aq} \xrightarrow{N_2O} \mathrm{N_2} + \mathrm{O^-} \qquad (1)$$



$$\mathrm{Fc(CH_2)_2COO^-} \xrightarrow{h\nu} \left[\mathrm{Fc(CH_2)_2COO^-}\right]^{\star} \begin{cases} \xrightarrow{a} \mathrm{Fc(CH_2)_2COO^-} \\ \xrightarrow{b,\ N_2O} \mathrm{Fc(CH_2)_2COO^-} + \mathrm{N_2} + \mathrm{O^-} \end{cases}$$

Flash photolysis studies of deaerated solutions showed negligible transient absorption in the red region, attributable to the solvated electron (720 nm) or to the anion of II (620 nm), thus eliminating mechanism 1. Using solutions containing N_2O, a sharp and permanent increase in absorption was found immediately after the flash in both the wavelength ranges, 600—650 nm and 320—360 nm, indicating the anion of II is produced during the flash when N_2O is present. Also, the magnitude of the absorption increase at 625 nm produced by one flash of fixed energy varied with N_2O concentration in a manner in quantitative agreement with mechanism 2. From the reciprocal plot, k_1/k_2 was found to be 1.9×10^{-4} and since $k_2 \leqslant 7.4 \times 10^9$ $M^{-1}s^{-1}$, we may deduce that the lifetime of the photoexcited state in the absence of N_2O, $k_1^{-1} \geqslant 0.7$ μs. However, with our present apparatus we do not observe any transient absorptions in the absence of N_2O and so cannot characterise this excited state.

The corresponding photo-oxidation and reduction reactions are also found to occur with 4-ferrocenylbutanoic and 5-ferrocenylpentanoic acids.

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