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PHOTOCHEMICALLY INDUCED ELECTRON TRANSFER FROM [3]FERROCENOPHANYLBUTANOATE ANIONS

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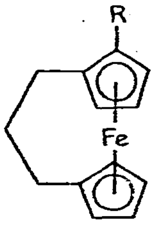
Summary

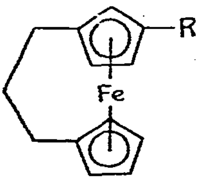
The anions of 4-([3]ferrocenophanyl)butanoic acids (Id and IId), when excited by light of around 240 nm wavelength in aqueous solution in the presence of N_2O, undergo photo-oxidation to zwitterions (III and IV respectively) in a manner completely analogous to the reaction of 4-ferrocenylbutanoate anion. The differences in the kinetic parameters of the reactions are thought to be attributable in part to slight tilting of the cyclopentadienyl rings caused by the connecting trimethylene bridge.

Previous work [1,2,3] on (ω-carboxyalkyl)ferrocenes has shown that excitation with light of around 240 nm wavelength produces a photo-excited state, presumed to be a triplet, with a lifetime greater than 1 μs, which may transfer an electron to N_2O and which is quenched by alcohols. Since the half-wave potentials for polarographic oxidation of [m]ferrocenophanes (m = 2-5) vary [4] in a manner which suggests that cyclopentadienyl ring-tilting leads to an increase in the ease of one-electron oxidation of the substrate, it was of interest to carry out similar photochemical studies on (carboxyalkyl)-

[3]ferrocenophanes for which a modest degree of ring-tilting is likely to obtain [5]. Although minimal differences were expected in the ease of oxidation or in the electronic spectra of the resulting ferricenium ions, it was thought possible that the kinetic parameters of the triplet states might be appreciably different.

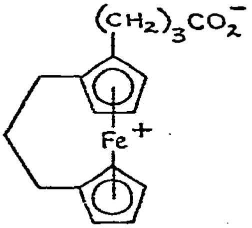


(I)

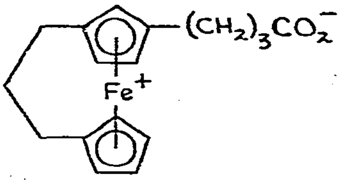


(II)

a; $R = CO(CH_2)_2CO_2H$
b; $R = CO(CH_2)_2CO_2Me$
c; $R = (CH_2)_3CO_2Me$
d; $R = (CH_2)_3CO_2H$



(III)



(IV)

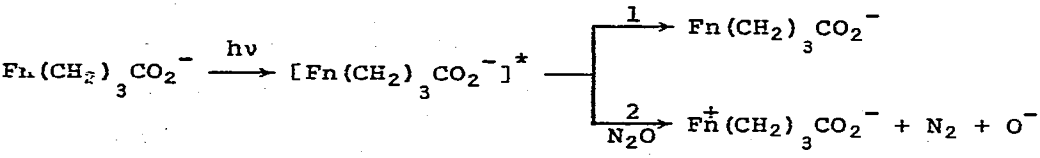
The required acids (Id) and (IId) were prepared by a modification of the route described [6] by Moise et al. Friedel-Crafts reaction of [3]ferrocenophane (I; R = H) with succinic anhydride/aluminium chloride in dichloromethane gave a mixture of the isomeric keto-acids (Ia) and (IIa) which was converted, without separation, into the corresponding methyl esters (Ib) and (IIb) on treatment with acidified methanol. These esters were separated cleanly by chromatography (Al_2O_3) and their structures were readily apparent from their ^1H n.m.r. spectra (see Experimental). Clemmensen reduction of each keto-ester, using a two-phase benzene/methanol/HCl aq. solvent system, gave the corresponding saturated esters (Ic) and (IIc) which were converted into the acids (Id) and (IId) respectively by reaction with methanolic potassium hydroxide followed by acidification.

Results and Discussion

Aqueous solutions of the β-acid (IId) as the anion were prepared in borax buffer of pH 9. When N_2O was added after deaeration, illumination with light of 254 nm from a low pressure mercury arc lamp caused spectral changes in the solution which did not occur in the absence of N_2O. After extraction of the unreacted acid, the solution showed the familiar "ferricenium" peaks at 255 and 625 nm, in a spectrum almost identical to that obtained [1,2,3] from the photolysis of (ω-carboxyalkyl)ferrocenes under the same conditions. This spectrum was attributed to the zwitterion (IV), an assignment supported by the fact that the addition of titanium(III) chloride caused reduction back to (IId). On repeating these experiments with the α-isomer (Id), the results were found to be similar in all respects and consistent with the production of the zwitterion (III).

Flash photolysis experiments were carried out, using the system previously described [7], in which the absorbance change at a selected wavelength was measured for a flash of chosen energy. Using solutions 1×10^{-4} M in (IId), with 2×10^{-2} M N_2O added, it was found that no absorbance change at 625 nm was produced when the filter compartment of the cell contained 5×10^{-3} M benzoic acid and that when it contained 15% aqueous acetic acid, the absorbance change was only 15% of that produced when the filter compartment was filled with distilled water. Thus it may be deduced that the effective light of the flash is mostly in the range below 245 nm.

Using similar solutions of (IId), the absorbance increase at 625 nm produced by a flash of constant energy was measured as a function of $_2O$ concentration. A slight increase was observed with increasing N_2O concentration which, when interpreted by the following scheme yielded, from the plot of the reciprocal of the absorbance increase against reciprocal N_2O concentration, the conclusion that the ratio $k_1/k_2 = 2.7(\pm 1.5) \times 10^{-4}$ M.



$$Fn(CH_2)_3CO_2^- \xrightarrow{h\nu} [Fn(CH_2)_3CO_2^-]^* \begin{cases} \xrightarrow{1} Fn(CH_2)_3CO_2^- \\ \xrightarrow[N_2O]{2} \overset{+}{Fn}(CH_2)_3CO_2^- + N_2 + O^- \end{cases}$$

(Fn = β-[3]ferrocenophanyl)

In other experiments, the concentration of N_2O was kept constant and the absorbance increase at 625 nm was measured as a function of methanol concentration. The general effect was similar to that previously observed [2] for (2-carboxyethyl)ferrocene, but it was found that a lower concentration of alcohol sufficed to bring about the same decrease in the absorbance change. Invoking reaction (3) as the cause of this decrease

$$[Fn(CH_2)_3CO_2^-]^* \xrightarrow[ROH]{3} Fn(CH_2)_3CO_2^-$$

we obtain equation (i):

$$\frac{1}{\phi\{\overset{+}{Fn}(CH_2)_3CO_2^-\}} = \frac{1}{\phi\{[Fn(CH_2)_3CO_2^-]^*\}}\left[1+\frac{k_1}{k_2[N_2O]}+\frac{k_3[ROH]}{k_2[N_2O]}\right] \qquad (i)$$

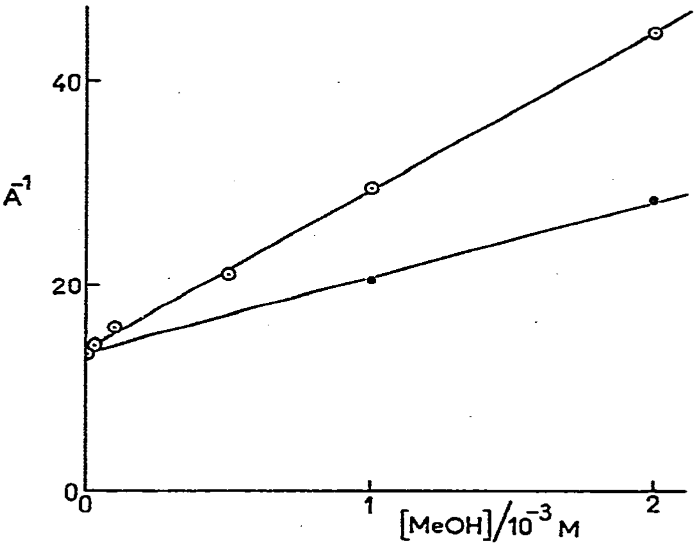


Figure 1. Plot of the reciprocal of the absorbance increase at 625 nm produced by a flash of 442J in a solution containing 10^{-2} M borax, 1.23×10^{-2} M N_2O and 1×10^{-4} M 4-(β-[3]ferrocenophanyl)butanoate, against the concentration of CH_3OH (⊝) or CD_3OD (●).

Figure 1 shows that our data, for both methanol and perdeuteromethanol, are consistent with equation (i). From the best straight lines, it is found that $k_3/k_2 = 14.0$ for CH_3OH and 6.7 for CD_3OD. It may be noted that since the constant N_2O concentration was far in excess of k_1/k_2, these values for the ratio k_3/k_2 do not rely heavily on that quoted above for k_1/k_2.

With 4-ferrocenylbutanoate ion, the value of k_3/k_2 from adding CH_3OH was found [2] to be 3.1 and, interpolating the data [2] for 3-ferrocenylpropanoate and 5-ferrocenylpentanoate, a value of about half this would be expected for CD_3OD. Thus the alkyl bridge, while having no influence on the kinetic isotope effect, causes the rate constant ratio to be significantly altered.

Similar series of experiments were carried out on the α-isomer (Id), leading to fairly comparable results. From the variation of the absorbance change with N_2O concentration, the value of $1.2(\pm 0.7) \times 10^{-4}$ M was obtained for k_1/k_2. From the experiments with constant N_2O concentration and variable amounts of added alcohol, the ratio k_3/k_2 was found to be 10.0 for CH_3OH and 5.6 for CD_3OD.

As demonstrated previously [1,2], since the maximum possible rate for reaction (3) would be that of a diffusion-controlled process, k_3 is most unlikely to exceed 10^{10} M^{-1} s^{-1} and so, from the results for (IId), $k_2 \leq 7 \times 10^8$ M^{-1} s^{-1} and $k_1 \leq 1.9 \times 10^5$ s^{-1}. Thus, for the lifetime of the photoexcited state, $[Fn(CH_2)_3CO_2^-]^*$, obtained from the β-substituted compound, we have, as a minimum value, $k_1^{-1} \geq 5$ μs.

For the two isomers, (Id) and (IId), some variation is found in the values for k_1/k_2, but this difference may not be significant since both of these are deduced by measuring rather small differences in the absorbance change and these reciprocal plots tend to show appreciable scatter. In addition, both values lie in the general range found [2,3] for the series, $Fc(CH_2)_nCO_2^-$ (where Fc = ferrocenyl) for n = 1 to 4.

However, there does appear to be a significant difference in the values of k_3/k_2 for the two isomers, which could be attributable to the varying effects of the slight tilting of the cyclopentadienyl rings, depending on the position of substitution of the ω-carboxyalkyl group. But it would be inappropriate wholly to attribute the kinetic variations, either between (Id) and (IId), or the more significant differences between either and 4-ferrocenylbutanoate, to the tilting effect which trimethylene bridging exerts on the cyclopentadienyl rings, since the bridging group may also generate electronic effects. To help in differentiating these, it is intended to study the photochemical behaviour of α,1'- and β,1'-diethyl derivatives of 4-ferrocenylbutanoic acid. For such compounds, the electronic effects of the ethyl substituents would closely resemble those of the trimethylene bridges in (Id) and (IId) but ring-tilting effects would be absent.

Experimental

All preparative reactions were carried out under an atmosphere of pure, dry N_2. ^1H N.m.r. spectra were recorded for $CDCl_3$ solutions using a Perkin-Elmer R12A spectrometer at 60MHz using Me_4Si as internal reference. Melting points were determined in sealed, evacuated capillaries and are uncorrected. Petrol refers to the light petroleum fraction b.p. 40-60°. Chromatographies were carried out using Spence Grade H alumina which had been partially deactivated by exposure to the atmosphere for 6h. Yields of product are based on unrecovered starting material.

Succinoylation of [3]ferrocenophane

A suspension of finely powdered succinic anhydride (1.5 g; 15 mmol) in CH_2Cl_2 (50 ml) was added slowly to a well-stirred solution of [3]ferrocenophane [8] (3.5 g; 15 mmol) in CH_2Cl_2 (100 ml) containing finely ground aluminium chloride (2.7 g; 20 mmol). The mixture was stirred overnight, then poured into water, and the CH_2Cl_2 layer was separated and combined with two CH_2Cl_2 extracts of the aqueous layer. The total CH_2Cl_2 extract was then extracted with three portions of dilute NaOH aq. solution. From the CH_2Cl_2 solution there was obtained [3]ferrocenophane (0.73 g; 21% recovery). The alkaline extract was acidified with dilute HCl aq. and extracted thoroughly with CH_2Cl_2. The CH_2Cl_2 extract was washed (H_2O), dried ($MgSO_4$), and evaporated, giving a mixture of the keto-acids (Ia) and (IIa) (total yield 1.88 g; 47%) as an orange solid. This mixture was used without further purification.

Preparation of keto-esters (Ib) and (IIb)

Conc. H_2SO_4 (10 drops) was added to a solution of the keto-acid mixture (previous experiment) in methanol (150 ml). The mixture was refluxed for 16 h, then diluted with water (500 ml), and extracted thoroughly with CH_2Cl_2. The CH_2Cl_2 extract was washed with three portions of dilute NaOH aq. solution, then with water, dried ($MgSO_4$), and evaporated. The residual oil was dissolved in a little benzene and chromatographed. Petrol/ether (9/1) eluted the keto-ester (Ib) (0.45 g; 23%), a dark brown oil (lit. [6] oil); ^1H n.m.r. τ5.38 (1H; t), 5.62-5.80 (2H; m), and 5.9-6.2 (4H; m) (cyclopentadienyl protons), 6.32 (3H; s; OMe), and 6.8-8.1 (10H; m; methylene protons). Petrol/ether (4/1) eluted the keto-ester (IIb) (1.15 g 59%), a dark red-brown solid, m.p. 78-80° (lit. [6] 81°); ^1H n.m.r. τ5.36 (2H; d), 5.60-6.00 (4H; m), and 6.05-6.15 (1H; m) (cyclopentadienyl protons), 6.32 (3H; s; OMe), 6.80-7.55 (4H; m; $COCH_2CH_2CO$), and 8.04 (6H; bs; bridge protons).

Preparation of 4-(β-[3]ferrocenophanyl)butanoic acid (IId)

A solution of the keto-ester (IIb) (1.0 g; 3 mmol) in benzene (34 ml) was added to a flask containing freshly prepared zinc amalgam (10 g), water (34 ml), and conc. HCl aq. (34 ml), and the two-layer system was heated to reflux for 18 h. The liquid was then decanted from the residue and combined with benzene washings of the residue. The benzene layer was separated, combined with two benzene extracts of the aqueous layer, washed (H_2O), dried ($MgSO_4$), and evaporated, giving the ester (IIc) (0.68 g; 71%) as a yellow oil which was used without further purification; ^1H n.m.r. τ5.85-6.30 (7H; m; cyclopentadienyl protons), 6.35 (3H; s; OMe), 7.50-8.00 (6H; m) and 8.10 (6H; bs) (methylene protons).

The crude ester was dissolved in methanol (25 ml), a solution of KOH in methanol (20% w/v; 5 ml) was added, and the mixture was allowed to stand overnight, then diluted with water (100 ml), and extracted thoroughly with ether (to remove unchanged ester). The alkaline solution was made just acidic by addition of HCl aq., and extracted with three portions of ether. The total extract was washed (H_2O), dried ($MgSO_4$), and evaporated giving the acid (IId) (0.49 g; 75%) as a viscous yellow liquid. The compound crystallised from aqueous methanol, m.p. 98-100° (lit. [6] 101-102°).

Preparation of 4-(α-[3]ferrocenophanyl)butanoic acid (Id)

Clemmensen reduction of the keto-ester (Ib) and hydrolysis of the resulting saturated ester (Ic) were carried out exactly as described in the previous experiment. The acid (Id), which was obtained in 50% overall yield, crystallised on standing as a yellow solid, m.p. 120-122° (lit. [6] 120°).

Photochemical procedures

In all work, triply distilled water was used and all vessels with which the solutions came into contact had previously been carefully cleared with Decon and then rinsed 30 times with distilled water. Nitrous oxide was B.O.C. anaesthetic grade and was purified by trap-to-trap distillation and by degassing immediately before use. AnalaR borax and methanol were used and the perdeuteromethanol was supplied by Ryvan.

The flash photolysis apparatus, previously described [7], employed a cylindrical quartz cell of 200 mm path length, around which was a co-axial compartment for a filter solution to remove a selected part of the wavelength range of the photoflash. Since in these experiments with N_2O present, a smaller absorbance change was always observed on flashing with the same energy for a second time, all the data reported or used here relate to the first flash performed on a sample. Flashing was carried out with the solution and the contents of the filter compartment (distilled water unless otherwise stated) at 20°C.

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