Electron-transfer from Excited Carboxyalkylferrocenes to Nitrous Oxide

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When the anion $Fc[CH_2]_nCO_2^-$ (n = 2, 3, or 4) is illuminated, in aqueous solution containing nitrous oxide, with light of wavelength *ca.* 240 nm, a compound is obtained whose electronic spectrum resembles that of the ferricenium ion and which may be chemically reduced to the original acid. The structure assigned is that of the dipolar ion, $Fc^+[CH_2]_nCO_2^-$ (2). Addition of an alcohol diminishes the yield of (2), in a manner consistent with a photoexcited state undergoing three competitive processes; first-order decay to the ground electronic state, reaction with nitrous oxide to give (2), and quenching by ROH. It is deduced that the lifetime of this photoexcited state is greater than 1 μs, implying that it is probably a triplet state.

In view of the low ionization potential of ferrocene (FcH), its photoionization in solution is eminently feasible on energetic grounds, but previous studies[1] have shown no evidence, direct or indirect, for the occurrence of the process $FcH \xrightarrow{h\nu} FcH^+ + e^-$. One interpretation is that the excitation produced by 254 nm light is of a type which, unlike the CTTS absorption in

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[1] J. A. Powell and S. R. Logan, *J. Photochem.*, 1974, **3**, 189.

halides, does not facilitate ionization. However, in the cases of hexacyanoferrate(II) ion[2] and phenolate ion,[3] efficient photoionization occurs, although the excitation is not of the CTTS type.

We therefore resolved to study the photochemical behaviour of carboxyalkylferrocenes, $\mathrm{Fc[CH_2]_{\mathit{n}}CO_2^-}$, in which photoionization appears more probable since the carboxylate allows the molecule to be dissolved in a solvent as polar as water and also gives it a negative charge. Two methylene groups would suffice to minimise any electronic interaction between the ferrocenyl group and the carboxylate, so that the absorption processes, like those of alkylferrocenes, are virtually those of the ferrocene nucleus.

As has been already reported,[4] the u.v. illumination of 3-ferrocenylpropanoate ion in aqueous solution containing nitrous oxide leads to its photo-oxidation to 2-carboxyethylferricenium. We present here a fuller account of this work and of the mechanism involved.

EXPERIMENTAL

Preparative.—3-Ferrocenylpropanoic acid was prepared from ferrocene *via* formylferrocene[5] and ferrocenylacrylic acid,[6] which was hydrogenated.[5] 4-Ferrocenylbutanoic acid was prepared by Clemmensen reduction[7] of 3-ferrocenylcarbonylpropanoic acid[8] and 5-ferrocenylpentanoic acid by an analogous route.

Sample Handling.—Aqueous solutions were made up in doubly distilled water. Cell assemblies, both for continuous illumination and for flash photolysis experiments, had attached a bulb to facilitate the degassing of the solution by five freeze–pump–thaw cycles. The vacuum line was also equipped to saturate degassed solutions with $\mathrm{N_2O}$ at a known pressure and to collect and measure the yield of permanent gases produced in any experiment.

The quartz cells used for irradiation were 50 mm diam. × 20 mm path length for the continuous illumination and 15 mm diam. × 200 mm path length for flash photolysis. The former were irradiated with either an Engelhard Hanovia low-pressure mercury lamp emitting principally at 253.7 nm or a Philips cadmium lamp emitting at 228.8 nm, and the intensities of these lines were determined by ferrioxalate actinometry. The cells for flash photolysis incorporated a concentric filter compartment into which could be put a filter solution which transmitted the desired wavelength range of the photo-flash. Other details of the flash photolysis system were as previously described.[9]

RESULTS

3-Ferrocenylpropanoic acid was dissolved as the anion (1) in aqueous borax buffer at pH 9. When deaerated solutions were illuminated with u.v. light, whether of wavelength 254 or 229 nm by steady illumination or of wavelengths around 250 nm from the flash tubes, no change was detected subsequently in the absorption spectrum. When nitrous oxide was added to the solutions with concentrations in the region of 10^{-2} mol dm^{-3}, u.v. illumination caused the solutions to turn bluish green and the spectrum showed new absorption bands at 255 and 620 nm, with the intensity of the former being *ca.* 40 times the greater. This spectrum resembles that of the ferricenium ion. Nitrogen was produced concurrently with this ferricenium compound. Thus it appeared that the overall reaction could be represented as in equation (i). Since similar results were obtained by using unbuffered solutions with pH in the range 7—11, the borax contributes nothing to this process.

$$\underset{(1)}{\mathrm{Fc[CH_2]_2CO_2^-}} + \mathrm{N_2O} \xrightarrow{h\nu} \underset{(2)}{\mathrm{Fe^+[CH_2]_2CO_2^-}} + \mathrm{N_2} + \mathrm{O^-}(\xrightarrow{\mathrm{H^+}} \mathrm{OH}) \quad \text{(i)}$$

To check the above assignment for the product, a solution of (1) (10^{-2} mol dm^{-3}) in aqueous borax was illuminated with stirring for 60 h, to obtain a substantial yield of product. When the solution was acidified and extracted with dichloromethane, the blue colour remained in the aqueous phase and the organic layer was found to contain only unchanged acid. Addition of titanium(III) chloride to the aqueous phase dissipated the blue colouration. Extraction of this (acid) solution with dichloromethane led to the isolation of a single yellow solid, identified as the original acid on the basis of its m.p., its R_F value (t.l.c. on silica gel plates; benzene–ether), and its i.r. spectrum. Thus the blue compound was the dipolar ion 2-carboxyethylferricenium (2).

Attempts were made to resolve the stoicheiometry of the reaction, with regard to the fate of the hydroxyl radical. It is conceivable that this oxidises another substituted ferrocene to ferricenium, in which case one molecule of nitrogen would be produced for every *two* of the ferricenium species. Accurate comparison of the product yields proved difficult, principally because it was feasible to obtain only rather low yields of the products in view of the very intense absorption of (2) at the wavelength of excitation. If the irradiation was prolonged, it appeared that the product (2) was undergoing photoreaction; introducing a magnetic stirrer to diminish the internal filter effect of the product served to increase the error in estimating the nitrogen yield. For each molecule of nitrogen produced, the product of the number of dipolar ions (2) and their extinction coefficient at 255 nm was found to be $13\,500 \pm 1\,500$ dm^3 mol^{-1} cm^{-1}. Since, for the ferricenium ion[10] itself,

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[2] M. Shirom and G. Stein, *J. Chem. Phys.*, 1971, **55**, 3372.

[3] J. Feitelson, E. Hayon, and A. Treinin, *J. Amer. Chem. Soc.*, 1973, **95**, 1025.

[4] E. K. Heaney and S. R. Logan, *J. Organometallic Chem.*, 1976, **104**, C31.

[5] M. Rosenblum, A. K. Banerjee, N. Danieli, R. W. Fish, and V. Schlatter, *J. Amer. Chem. Soc.*, 1963, **85**, 322.

[6] G. D. Broadhead. J. M. Osgerby, and P. L. Pauson, *J. Chem. Soc.*, 1958, 650.

[7] K. L. Rinehart, R. J. Curby, D. H. Gustafson, K. G. Harrison, R. E. Bozak, and D. E. Bublitz, *J. Amer. Chem. Soc.*, 1962, **84**, 3268.

[8] K. L. Rinehart, R. J. Curby, and P. E. Sokol, *J. Amer. Chem. Soc.*, 1957, **79**, 3423.

[9] E. K. Heaney, S. R. Logan, and J. A. Powell, *J.C.S. Faraday I*, 1977, 669.

[10] M. Rosenblum, 'Chemistry of the Iron Group Metallocenes,' Part 1, Wiley, New York, 1965, p. 41.

$\varepsilon_{250} = 12\,000\ dm^3\ mol^{-1}\ cm^{-1}$, this probably means that the OH radicals do not, in general, oxidise (1) to (2).

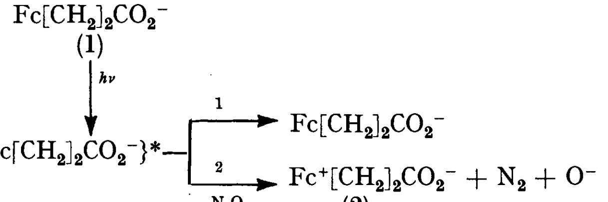
There are two obvious possibilities for the mechanism of the reaction summarised in equation (i), namely (A) electron photo-ejection from (1), followed by scavenging of the (solvated) electron by nitrous oxide and (B) direct electron transfer from a photoexcited state of (1) to nitrous oxide.

Mechanism (A)

$$\underset{(1)}{Fc[CH_2]_2CO_2^-} \xrightarrow{h\nu} \underset{(2)}{Fc^+[CH_2]_2CO_2^-} + e^-_{aq}$$

$$e^-_{aq} + N_2O \longrightarrow N_2 + O^-$$

Mechanism (B)



These mechanisms predict distinct consequences for simple flash photolysis experiments. For flashing a deaerated solution, mechanism (A) predicts that transient absorptions would be seen, due to e^-_{aq} ($\lambda_{max.}$ 720 nm) and the dipolar ion (2), whereas (B) predicts that neither of these would be detected. In the presence of nitrous oxide, both predict a persisting increase in absorption concomitant with the flash, due to the formation of (2).

Flash photolysis studies of solutions of (1) in borax buffer at pH 9 containing nitrous oxide showed, as expected, a considerable increase in absorption during the flash, in the wavelength ranges 600—650 nm and below 360 nm. In deaerated solutions, no transient absorption was observed at the red end of the spectrum, thus eliminating mechanism (A).

When a solution sample was subjected to successive flashes of the same energy, the increase in absorbance at 625 nm steadily diminished, presumably because of an inner filter effect. Thus, for quantitative work, the absorbance changes on subsequent flashes would not be comparable with those of first flashes. To test whether first flash data might also exhibit this effect, a series of experiments was conducted with constant acid concentration and constant nitrous oxide concentration; the increase in absorbance at 625 nm produced by the first flash was directly proportional to the flash energy over the range 150—600 J. Thus, all quantitative data refer to ' first flash ' experiments.

As a necessary consequence of mechanism (B) we have equation (ii). To test this relationship, a series of experiments was carried out in which the increase in absorbance at 625 nm produced by a flash of constant energy (442 J) was measured as a function of nitrous oxide concentration. As shown in Figure 1, these results are consistent with equation (ii). From the ratio of slope to intercept of the regression line, the ratio k_1/k_2 was determined as 1.8 (±0.6) × 10^{-4} mol dm^{-3}.

$$\frac{1}{\phi(Fc^+[CH_2]_2CO_2^-)} = \frac{1}{\phi(\{Fc[CH_2]_2CO_2^-\}^*)}\left\{1 + \frac{k_1}{k_2[N_2O]}\right\} \quad \text{(ii)}$$

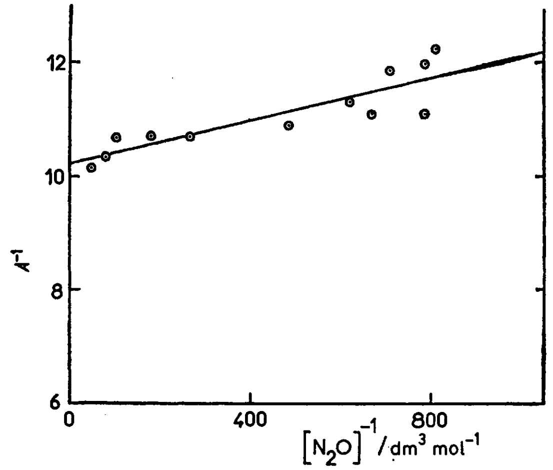


FIGURE 1 Plot of the reciprocal of the absorbance change at 625 nm against the reciprocal of the nitrous oxide concentration from a series of experiments using solutions 2.5 × 10^{-4}M in 3-ferrocenylpropanoate and 10^{-2}M in borax, at 20 °C, flashed at an energy of 442 J

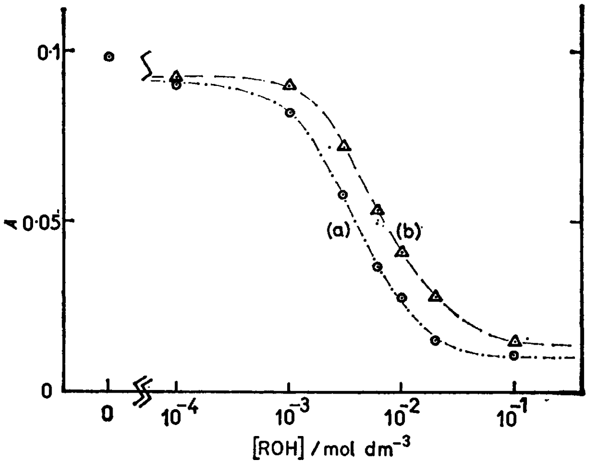


FIGURE 2 Plots of the absorbance change at 625 nm against the alcohol concentration from series of experiments using solutions 2.5 × 10^{-4}M in 3-ferrocenylpropanoate, 10^{-2}M in borax and 1.2 × 10^{-2}M in N_2O, at 20 °C, flashed at an energy of 442 J: (a) CH_3OH; (b) CD_3OD

To determine what wavelength range of light from the photoflash was responsible for the observed photoeffects, other solutions were substituted in the filter compartment for the distilled water. With aqueous 15% acetic acid, which limits transmission to wavelengths greater than *ca.* 240 nm, the absorbance increase at 625 nm was about a quarter of that observed with water, whereas with 5 × 10^{-3} mol dm^{-3} benzoic acid, which transmits only light of wavelength greater than *ca.* 290 nm, no absorbance change was detected. Thus the effective radiation must be chiefly in the region 230—245 nm.

Addition of an alcohol to the solution along with the nitrous oxide diminished the absorbance change on flashing. The results, for methanol and [$^2H_4$]methanol, are shown in Figure 2. The curve for [$^2H_4$]methanol can be regarded as a sideways displacement of the curve for methanol, consistent with the effect of a given concentration of methanol being the same as that of a constant times that concentration of [$^2H_4$]methanol where the value of the constant is close to 2.0. The relative efficiencies of other alcohols in diminishing the absorbance change are indicated by the data in Table 1, which shows that ethanol and propan-2-ol are more effective than equal concentrations of methanol, but t-butyl alcohol is less effective than methanol.

TABLE 1

Effect of various alcohols (ROH) on the increase in absorbance at 625 nm on flashing (442 J) an aqueous solution 2.5×10^{-4}M in $Fc[CH_2]_2CO_2^-$, 10^{-2}M in borax, and 1.2×10^{-2}M in N_2O

	Absorbance increase as fraction of that with no alcohol			
[ROH]:	10^{-3}M	10^{-2}M	10^{-1}M	1M
MeOH	0.89	0.30	0.12	0.18
CD_3OD	0.98	0.46	0.17	0.24
EtOH	0.63	0.19	0.10	0.07
Pr^nOH	0.62	0.35	0.28	0.21
Pr^iOH	0.60	0.26	0.15	0.12
Bu^tOH	0.97	0.73	0.62	0.47

Selected experiments with 4-ferrocenylbutanoic (3) and 5-ferrocenylpentanoic (4) acids established that the results depended little on whether the number of methylene groups between the ferrocene and the carboxylate was 2, 3, or 4. With each of the above acids, similar effects were observed on illuminating in the presence of nitrous oxide. With each, the corresponding blue compound was separated and reduced to an acid identical, on the basis of m.p., i.r. spectrum, and t.l.c., with the original one. With each acid, the effect of nitrous oxide concentration on the absorbance change produced by one flash was investigated and plots were obtained similar to Figure 1. From these it was deduced that k_1/k_2 was, for (3), $1.1(\pm0.5) \times 10^{-4}$ and, for (4), $1.4(\pm0.6) \times 10^{-4}$ mol dm^{-3}.

As shown by the data in Table 2, the effect of methanol on the anions of (3) and (4) closely parallels that with (1). Also, with (4), [$^2H_4$]methanol was less efficient, by a factor of 2.0, in diminishing the absorbance change on flashing, so that the fuller results for (4) closely resemble those for (1) shown in Figure 2. Other experiments with (3) and (4) using ethanol also illustrated that the effect of alcohol is virtually independent of the number of methylene groups between the ferrocenyl and the carboxylate.

TABLE 2

Effect of methanol on the increase in absorbance at 625 nm on flashing (442 J) an aqueous solution 2.5×10^{-4}M in the acid, 10^{-2}M in borax, and 1.2×10^{-2}M in N_2O

	Absorbance increase as fraction of that with no alcohol			
[MeOH]:	10^{-3}M	10^{-2}M	10^{-1}M	1M
$Fc[CH_2]_3CO_2H$ (3)	0.74	0.27	0.19	0.16
$Fc[CH_2]_4CO_2H$ (4)	0.68	0.27	0.16	0.18

DISCUSSION

The results indicate that the anion $Fc[CH_2]_nCO_2^-$ does not undergo photoionization by either a monophotonic or a biphotonic process. The absence of the former is in contrast to phenolate; that of the latter excludes comparison with the series, $Ph[CH_2]_nCO_2^-$, in which one of the biphotonic processes is [11] photoejection, accompanied by decarboxylation.

The effect of the alcohols on the yield of (2) appears attributable to some process by which the triplet state is ' scavenged ' by ROH. Thus, with an alcohol present, mechanism (B) needs to be amended by the addition of this reaction (iii) with ROH. Consequently, the yield of (2) should now be given by equation (iii). Taking

$$\phi(\mathrm{Fc^+[CH_2]_2CO_2^-}) = \phi(\{\mathrm{Fc[CH_2]_2CO_2^-}\}^*)\left\{\frac{k_2[\mathrm{N_2O}]}{k_1 + k_2[\mathrm{N_2O}] + k_3[\mathrm{ROH}]}\right\} \quad \text{(iii)}$$

reciprocals, we obtain equation (iv). Thus, in a series

$$\frac{1}{\phi(\mathrm{Fc^+[CH_2]_2CO_2^-})} = \frac{1}{\phi(\{\mathrm{Fc[CH_2]_2CO_2^-}\}^*)} \left\{1 + \frac{k_1}{k_2[\mathrm{N_2O}]} + \frac{k_3[\mathrm{ROH}]}{k_2[\mathrm{N_2O}]}\right\} \quad \text{(iv)}$$

of experiments with a constant concentration of nitrous oxide and constant flash energy, the reciprocal of the absorbance increase at 625 nm [which is proportional to the quantum yield of (2)], should be a linear function of alcohol concentration. Equation (iv) is tested in Figure 3, which demonstrates acceptable linearity for the results with methanol and [$^2H_4$]methanol.

Taking the value of slope/intercept of the best straight lines in Figure 3, and substituting for nitrous oxide concentration and for the previously determined value of k_1/k_2, we obtain $k_3/k_2 = 3.65$ (CH_3OH) and 1.82 (CD_3OD), which are related by a factor of 2.0. As noted earlier, ethanol is slightly more efficient than methanol in reducing the yield of (2), and the plot corresponding to Figure 3 for ethanol gives $k_3/k_2 = 5.6$. For the other acids, the data with methanol yielded k_3/k_2 equal to 3.1 [for (3)] and 3.6 [for (4)]. For the latter, use of [$^2H_4$]methanol gave $k_3/k_2 = 2.0$.

Since, for all three acids, k_3/k_2 exceeds unity, the maximum possible value for k_1 would occur if reaction (iii) were diffusion controlled. Taking this limit as *ca.* 10^{10} dm^3 mol^{-1} s^{-1}, from the data for (1) and ethanol we have $k_1 \leq 0.32 \times 10^6$ s^{-1}, which would mean that the lifetime of the photoexcited state, $\{Fc[CH_2]_2CO_2^-\}^*$, is at least 3 ± 1 μs. For the acids (3) and (4), a similar

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[11] L. J. Mittal, J. P. Mittal, and E. Hayon, *J. Phys. Chem.*, 1973, **77**, 2267.

figure for the minimum lifetime is obtained even from the methanol data.

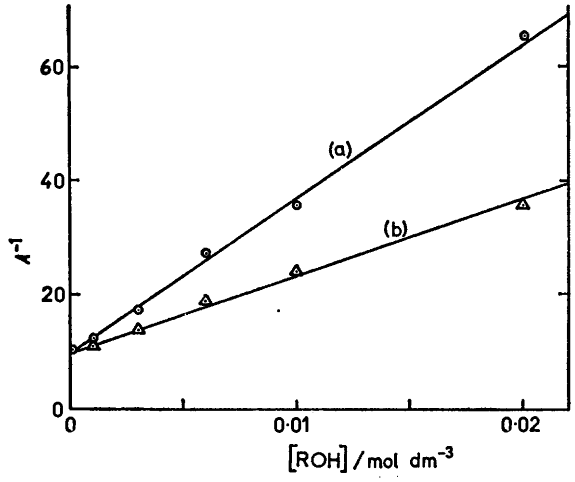

FIGURE 3 Plots of the reciprocal of the absorbance change at 625 nm against the alcohol concentration, for (a) CH_3OH and (b) CD_3OD, using the data of Figure 2

Since lifetimes of a few μs are more typical of triplet than of singlet states, it will be assumed (particularly since these are ***minimum*** values) that the photoexcited state represented by $\{Fc[CH_2]_nCO_2^-\}^*$ is a triplet. It is apparently produced most efficiently by light of wavelength less than 240 nm, since the yield of (2) is considerably diminished by excluding this range of wavelengths, even though the total actinic effect of the flash, as measured by the ferrioxalate actinometer, is scarcely affected [12] by using the acetic acid filter solution instead of water.

In quenching the triplets, methanol was more efficient than $[^2H_4]$methanol, by a factor of 2. The magnitude of this kinetic isotope effect makes it seem unlikely that the quenching reaction by methanol is close to the diffusion controlled limit, since that would imply an extremely large kinetic isotope effect in the intrinsic rate constants, corrected for diffusional effects. Thus the lifetimes of the triplets are perhaps rather greater than this minimum figure of 3 μs. The variations in the quenching rates of the different alcohols do not suffice to identify the quenching process, but it is probably chemical in nature, especially in view of the H/D kinetic isotope effect of at least a factor of 2.

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[6/2286 *Received, 16th December,* 1976]

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[12] E. K. Heaney and S. R. Logan, in preparation.