# Photo-oxidation of Ferrocenyl-substituted Carboxylic Acids

By **Elizabeth K. Heaney** and **S. R. Logan,*** School of Physical Science, New University of Ulster, Coleraine, N. Ireland

Photochemical studies have shown that the u.v. excitation of ferrocenylacetate ion (I) or of ferrocenoate ion (II) leads in each case to an excited state which may transfer an electron to an acceptor such as $N_2O$. The lifetime of these excited states are found to be at least 2 μs (I) and 0.07 μs (II). Unlike its higher homologues, the dipolar ion obtained by electron transfer from (I) is unstable, especially at high pH.

PREVIOUS studies [1] of the photochemistry of the carboxyalkylferrocenes $Fe(CH_2)_nCO_2^-$ ($n = 2$, 3, and 4) demonstrated that an electron may be readily transferred to an acceptor such as $N_2O$ from a photo-excited state whose lifetime exceeds 1 μs and which is probably a triplet state. The product, a carboxyalkylferricenium dipolar ion, is in all three cases stable and can easily be separated from the anion of the acid; its electronic spectrum resembles that [2] of the ferricenium ion.

Whereas the earlier work [1] demonstrated that lengthening of the alkyl chain in excess of two methylenes had a minimal effect on the behaviour of the anion, the triplet state, or the dipolar ion, a marked effect is to be expected when the number of methylenes is reduced to zero, since the electronic interaction between the ferrocenyl and the carboxylate is then maximized. Accordingly, similar studies were undertaken with ferrocenylacetic acid and with ferrocenoic acid.

## EXPERIMENTAL

*Preparative.*—Ferrocenylacetic acid was prepared *via* the tertiary amine $FcCH_2NMe_2$,[3] its methiodide,[4] and the nitrile [5] $FcCH_2CN$ the latter being hydrolysed. Ferrocenoic acid was prepared by the alkaline hydrolysis of diphenylcarbamoylferrocene which was obtained [6] by

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[1] E. K. Heaney and S. R. Logan, *J.C.S. Perkin II*, 1977, 1353.

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

[3] J. M. Osgerby and P. L. Pauson, *J. Chem. Soc.*, 1958, 656.

[4] J. K. Lindsay and C. R. Hauser, *J. Org. Chem.*, 1957, **22**, 357.

[5] D. Lednicer, J. K. Lindsay, and C. R. Hauser, *J. Org. Chem.*, 1958, **23**, 653.

[6] W. F. Little and R. Eisenthal, *J. Amer. Chem. Soc.*, 1960, **82**, 1577.

a Friedel–Crafts substitution using diphenylcarbamoyl chloride.

*Sample Handling*.—Aqueous solutions were made up in doubly distilled water. The cell assemblies were so designed as to facilitate the degassing of solutions by five cycles of freeze–pump–thaw. Other details of the cell dimensions and irradiation procedures [1] and of the flash photolysis apparatus [7] were as previously described.

*Actinometry*.—The intensity of the 254 nm light from the mercury lamp was measured *in situ* by ferrioxalate actinometry [8] using the techniques previously [9] described.

## RESULTS

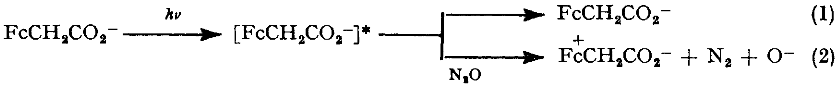
*Ferrocenylacetic Acid*.—When ferrocenylacetic acid was dissolved as the anion in aqueous solution and $N_2O$ added after deaeration, illumination with u.v. light caused the solution to turn bluish green, with new absorption bands appearing at 255 and 625 nm; this behaviour was previously observed for 3-ferrocenylpropanoate. By analogy with this earlier work, the change was attributed to the overall reaction:

$$\mathrm{FcCH_2CO_2^- + N_2O \xrightarrow{h\nu} Fc^+CH_2CO_2^- + N_2 + O^-\ (\xrightarrow{H^+} OH)} \qquad \text{(i)}$$

In other experiments, after producing a substantial concentration of the blue compound by prolonged irradiation, the solution was acidified and extracted with ether to remove the unchanged acid. Addition of titanium(III) chloride dissipated the blue colour and further extraction with ether produced a yellow organic layer. Analysis of this extract by t.l.c. (silica-gel plates, benzene–ether) showed the presence of only one compound, the $R_F$ value and colour of which corresponded to that of ferrocenylacetic acid.

When degassed solutions of ferrocenylacetic acid in $10^{-2}$ mol dm$^{-3}$ borax buffer (pH 9) were flashed, only very small transient absorptions were observed in the region of 550—650 nm and no transient was seen near 720 nm. Thus, as for the higher homologues, it was clear that reaction (i) did not come about by photo-ejection of an electron from the anion, since in that case the intense absorption of the solvated electron should have been detected.

From a series of experiments in which the concentration of $N_2O$ was varied, the absorbance increase at 625 nm appearing immediately after the first flash was measured and its reciprocal was found to be linearly related to that of $N_2O$ concentration (see Figure 1). This is consistent with the occurrence of reaction (i) by means of electron transfer from a photo-excited state of the anion to $N_2O$ (see Scheme) and from the values of slope and intercept it may be deduced that $k_1/k_2 = 1.7\ (\pm 0.5) \times 10^{-4}$ mol dm$^{-3}$, which is not significantly different from the values obtained [1] for the higher homologues.



$$\mathrm{FcCH_2CO_2^- \xrightarrow{h\nu} [FcCH_2CO_2^-]^*} \begin{cases} \longrightarrow \mathrm{FcCH_2CO_2^-} & (1) \\ \xrightarrow[N_2O]{} \mathrm{\overset{+}{Fc}CH_2CO_2^- + N_2 + O^-} & (2) \end{cases}$$

SCHEME

The addition of an alcohol to a solution containing the anion and $N_2O$ was found to cause a decrease in the absorbance produced at 625 nm by flashing. Assuming, as for the higher homologues, that the mechanism of this decrease involves the quenching of the photoexcited state by ROH, reaction (3), in competition with reactions (1) and (2), one can deduce equation (ii):

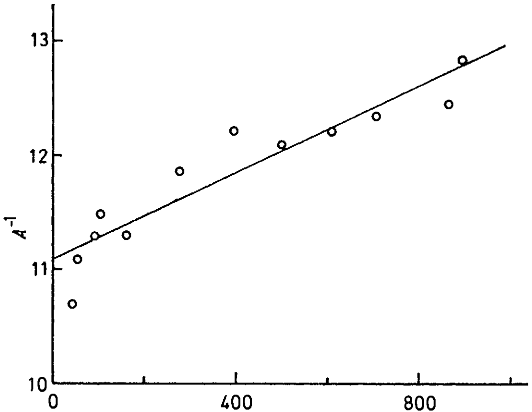


FIGURE 1 Plot of the reciprocal of the absorbance increase at 625 nm produced by the first flash, of energy 442 J, on a solution of $2.5 \times 10^{-4}$ mol dm$^{-3}$ ferrocenylacetic acid in $10^{-2}$ mol dm$^{-3}$ borax, against the reciprocal of the concentration of nitrous oxide

$$\mathrm{[FcCH_2CO_2^-]^* + ROH \longrightarrow FcCH_2CO_2^-} \qquad (3)$$

$$\frac{1}{\phi(\mathrm{\overset{+}{Fc}CH_2CO_2^-})} = \frac{1}{\phi(\{\mathrm{FcCH_2CO_2^-}\}^*)}\left\{1 + \frac{k_1}{k_2[\mathrm{N_2O}]} + \frac{k_3[\mathrm{ROH}]}{k_2[\mathrm{N_2O}]}\right\} \qquad \text{(ii)}$$

The data for the effect of methanol and [$^2H_4$]methanol are shown in Figure 2, in which both plots demonstrate acceptable linearity. From these, along with the previously determined value of $k_1/k_2$, the values of $k_3/k_2$ are deduced to be 4.1 ($CH_3OH$) and 2.2 ($CD_3OD$). It was also shown that ethanol had a slightly greater effect than methanol in reducing the absorbance rise, which would mean that for ethanol the value of $k_3$ is slightly greater. The addition of ethanol to degassed solutions not containing $N_2O$ had no effect on the small transient absorptions, which decayed within a few ms.

Whereas for the higher homologues,[1] the dipolar ion was quite stable, carboxymethylferricenium ion was found to decompose over a period of hours, or more rapidly in solutions of high alkalinity. This decay of the 625 nm absorption band, which was in all cases first order, was followed on the SP 500 spectrophotometer in the case of very slightly alkaline solutions, but for pH values between

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[7] E. K. Heaney, S. R. Logan, and J. A. Powell, *J.C.S. Faraday I*, 1977, 699.

[8] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.*, 1956, **A235**, 518.

[9] J. A. H. Cook and S. R. Logan, *J. Photochemistry*, 1974, **3**, 89.

12 and 13 it was followed for a few seconds after the flash using the flash photolysis apparatus. The data for the higher pH range are summarised in Figure 3, which shows that the first-order rate constant is directly proportional to the hydroxide ion concentration.

To clarify the decomposition products of the dipolar ion, samples of ferrocenylacetic acid in aqueous borax buffer containing $N_2O$ were irradiated with 254 nm light for long periods of time with internal stirring in order to produce substantial amounts of the dipolar ion. After acidification, the solution was extracted with ether to remove unused ferrocenylacetic acid. In one case the solution, still acid at *ca.* pH 2, was set aside until the blue colouration was no longer present. Extraction with ether then yielded a yellow solid, whose i.r. spectrum closely resembled that of authentic ferrocenylacetic acid, but which melted some 20 °C lower. T.l.c. (silica-gel plates, benzene–ether) showed the presence of two compounds, one with $R_F$ equal to ferrocenylacetic acid and a small amount of a more polar yellow compound.

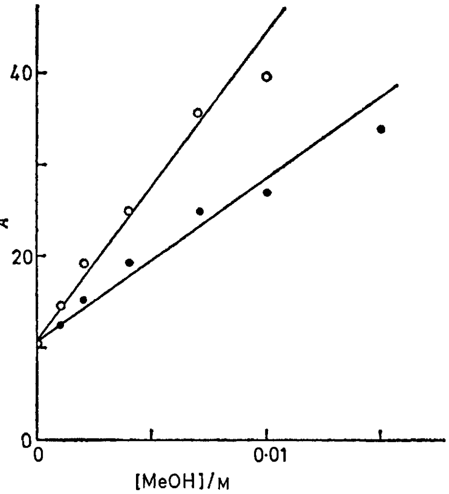


FIGURE 2 Plot of the reciprocal of the absorbance increase at 625 nm produced by the first flash, of energy 442 J, on a solution, $2.5 \times 10^{-4}$ mol dm$^{-3}$ in ferrocenylacetic acid, $10^{-2}$ mol dm$^{-3}$ in borax, $1.2 \times 10^{-2}$ mol dm$^{-3}$ in nitrous oxide and containing methanol (⊙) or perdeuteriomethanol (●), against methanol concentration

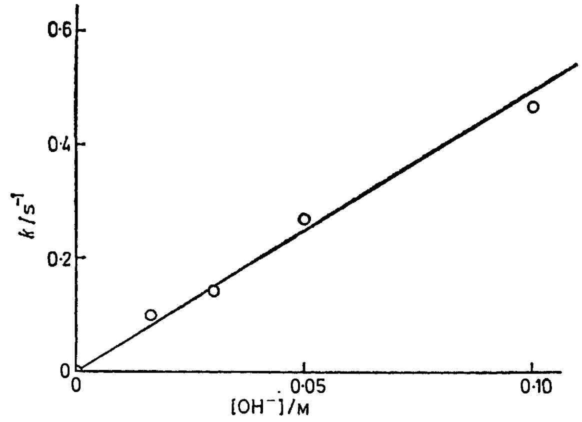


FIGURE 3 Plot of the first-order rate constant for the decay of the 625 nm absorption of the dipolar ion, $\overset{+}{Fc}CH_2CO_2^-$, against the concentration of hydroxide ion

In another experiment, the solution of the dipolar ion was made alkaline with aqueous KOH, which caused the blue colour to disappear. This solution was then left overnight before acidification and extraction with ether; very similar results were obtained, from which it was concluded that when the blue compound decomposed, whether in acid or in alkaline solution, it mostly underwent reduction back to ferrocenylacetic acid or its anion.

When a solution containing the dipolar ion was made alkaline it quickly changed colour from blue to yellow, but immediate reacidification of the solution caused the solution to turn bluish green. The electronic spectrum of the solution showed that the peaks at 255 and 625 nm had returned, but at somewhat reduced intensities. The spectrum of the solution just after it had been made alkaline showed neither of these peaks: in fact, it showed only a continuous decrease in absorbance from 225 nm upwards, with a weak shoulder at *ca.* 350 nm, but with no suggestion of a peak or even a shoulder at 440 nm, the wavelength at which all ferrocenes have a characteristic absorption.

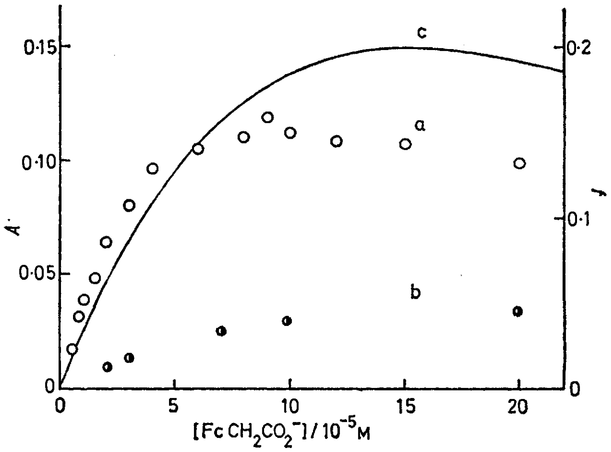


FIGURE 4 Plots, against ferrocenylacetic acid concentration, of (a) the absorbance increase at 625 nm produced by the first flash, of energy 442 J, in a solution of ferrocenylacetic acid in $10^{-2}$ mol dm$^{-3}$ borax containing $1.2 \times 10^{-2}$ mol dm$^{-3}$ nitrous oxide, (b) the absorbance increase when the filter compartment is filled with 15% aqueous acetic acid, and (c) the function $\varepsilon c\ 10^{-\varepsilon cl}$, taking $l$ as 0.8 cm and $\varepsilon$ as 3 533M$^{-1}$ cm$^{-1}$

A series of experiments was carried out in which the absorbance change at 625 nm produced by the first flash (of fixed energy) in a solution containing a fixed concentration of $N_2O$ was measured as a function of anion concentration. The results, shown in Figure 4, indicate that the maximum increase occurs at a concentration of just under $1 \times 10^{-4}$ mol dm$^{-3}$.

Since the increment of light, $-\mathrm{d}I$, absorbed within an increment of path length, $\mathrm{d}l$ is given by the equation:

$$-\mathrm{d}I/\mathrm{d}l = 2.303\ \varepsilon c I_0\ 10^{-\varepsilon cl} \qquad \text{(iii)}$$

it would follow that if the light which is effective in the photochemical process is either monochromatic or confined to a narrow range of wavelengths where $\varepsilon$, the decadic extinction coefficient, is constant, then the variation of the absorbance increase with concentration should be in proportion to the right-hand side of equation (iii). On

Figure 4 the function $\varepsilon c 10^{-\varepsilon c l}$ is also plotted, with $l$ taken as 8 mm and $\varepsilon$ as 3 533 $M^{-1}$ $cm^{-1}$. The discrepancy between these two curves indicates either a mistaken assumption or a neglect of some important factor. Another series of experiments using, in the filter compartment, not distilled water but 15% aqueous acetic acid solution, which transmits scarcely any light of wavelength less than 245 nm, was carried out and the results, also shown in Figure 4, demonstrate a totally different behaviour. Clearly the light which is effective in bringing about the reaction must extend over an appreciable range of wavelengths inclusive of 245 nm, which is a region where the extinction coefficient changes quite appreciably. Since this fact alone would result in considerable discrepancy between curves (a) and (c), other possible contributory causes need not be invoked.

*Ferrocenoic Acid*.—When degassed solutions of ferrocenoic acid containing $N_2O$ were irradiated with light of 254 nm, $N_2$ was obtained. Irradiation also produced a slight change in the u.v. spectrum, with an increase in absorbance over the range, 265—415 nm. Since there appeared to be no product which absorbed strongly (or at least, more strongly than the acid) at the wavelength of excitation, it was considered feasible to measure the quantum yield using continuous irradiation and without stirring, and to study its dependence on $N_2O$ concentration. For 254 nm light, $\phi(N_2)$ was found to increase from below 0.03 to greater than 0.04 as the $N_2O$ concentration was increased from $2 \times 10^{-3}$ to $2 \times 10^{-2}$ mol $dm^{-3}$.

A solution, $10^{-2}$ mol $dm^{-3}$ in ferrocenoic acid made up in $10^{-2}$ mol $dm^{-3}$ borax buffer, was saturated with $N_2O$ and irradiated with stirring for 30 h using 254 nm light. The solution, which had then turned a muddy brown, was acidified and then extracted with dichloromethane, leaving a brownish yellow aqueous layer, whose u.v. spectrum showed strong absorption throughout the range, with a peak at 255 nm. The addition of titanium(III) chloride caused only a slight change in colour but when followed by extraction, it was found that the organic layer was yellow and the aqueous one colourless. This product of the reduction was shown by t.l.c. to be ferrocenoic acid; no other product was detected by t.l.c. in the unchanged ferrocenoic acid which had previously been recovered in the initial extraction.

After a solution containing $N_2O$ was subjected to several flashes, the yield of $N_2$ was measured and it was calculated that, based on the amount of light of wavelengths less than 265 nm, the $N_2$ quantum yield was similar to that found using continuous illumination with 254 nm light. Thus it was concluded that $N_2$ was produced only from a monophotonic process and not, additionally, from a biphotonic process.

When degassed solutions of ferrocenoate in $10^{-2}$M borax buffer were flashed, transient absorptions lasting a few ms were observed over the range 400—800 nm. By using 15% aqueous acetic acid and $5 \times 10^{-3}$ mol $dm^{-3}$ benzoic acid solutions in the filter compartment instead of distilled water, it was deduced that whereas the wavelengths of the incident light responsible for these transients were both greater than and less than 245 nm, the range did not extend beyond 290 nm. It was also shown that the addition of $10^{-1}$ mol $dm^{-3}$ ethanol did not affect these transient absorptions.

When solutions of ferrocenoate ion in $10^{-2}$ mol $dm^{-3}$ borax buffer containing $N_2O$ were flashed, a blue colour could be seen in the cell, but it was readily dispelled. Over the range, 500—650 nm, small absorptions were detected, of which a portion decayed over a few ms and a portion persisted for at least a second. The interposition of the 15% aqueous acetic acid filter was found to prevent the occurrence of either, whereas the addition to the solution of $10^{-1}$ mol $dm^{-3}$ ethanol had little effect on the transient part of the absorption, but resulted in the occurrence of no persistent absorption.

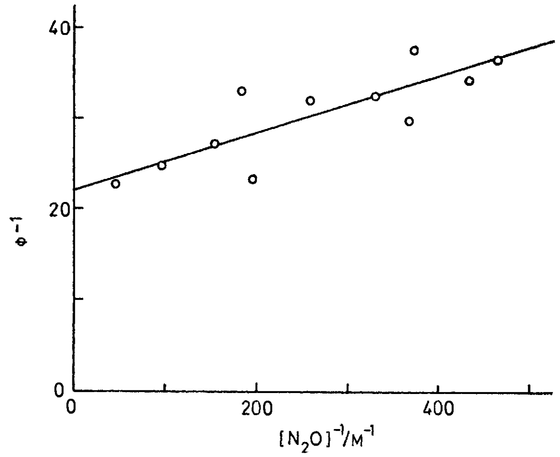


FIGURE 5 Plot of the reciprocal of the quantum yield of nitrogen against the reciprocal concentration of nitrous oxide for the irradiation with light of 254 nm of solutions of $2.5 \times 10^{-4}$ mol $dm^{-3}$ ferrocenoic acid in $10^{-2}$ mol $dm^{-3}$ borax

Since very little transient absorption is observed around 720 nm in the absence of $N_2O$ and no less in its presence, it is clear that the mechanism of the reaction must be analogous to that deduced previously for the carboxyalkylferrocenes. Thus, one has the equation (iv) which predicts

$$\frac{1}{\phi(N_2)} = \frac{1}{\phi\{(FcCO_2^-)^*\}}\left\{1 + \frac{k_1}{k_2[N_2O]}\right\} \qquad (iv)$$

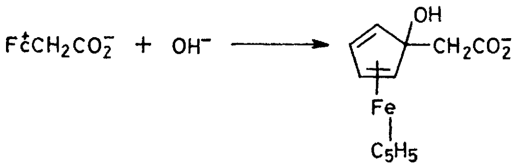
that the reciprocal of the quantum yield of $N_2$ should be linearly related to the reciprocal of the $N_2O$ concentration. This relationship is tested in Figure 5 using the data from continuous 254 nm irradiation referred to above; from the best straight line it may be deduced that $\phi\{(FcCO_2^-)^*\} = 0.045$ and that $k_1/k_2 = 1.4 (\pm 0.2) \times 10^{-3}$ mol $dm^{-3}$.

## DISCUSSION

The electron transfer process from ferrocenylacetate has been hypothesised as involving as an intermediate a photoexcited state, $\{FeCH_2CO_2^-\}^*$, and since the values of the rate constant ratios $k_1/k_2$ and $k_2/k_3$ are similar to those of the next homologue,[1] it may once again be shown that the lifetime of this excited state, $k_1^{-1}$, must be at least 2 μs and that it is most probably a triplet. As for the higher homologues, alcohols inhibit the formation of the blue compound and there is a kinetic isotope effect of almost 2 between the efficiencies of $CH_3OH$ and $CD_3OD$.

The observed decay of the dipolar ion in alkaline solution can only involve a bimolecular reaction with the hydroxide ion, since the rate is proportional to its concentration. Two possible reactions may be hypothesised, which are represented below:

$$\overset{+}{\mathrm{Fc}}\mathrm{CH_2CO_2^-} + \mathrm{OH^-} \longrightarrow \mathrm{FcCH_2CO_2^-} + \mathrm{OH} \qquad \text{(v)}$$

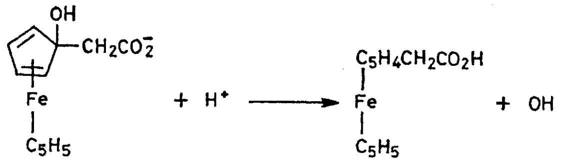


(vi)

If reaction (v) occurred, the subsequent fate of the OH radical is difficult to predict, but it would seem unlikely that it should remain readily available to participate in the reverse of reaction (v) when the pH is subsequently lowered. In any case, it is not at all clear if the OH radical would react with ferrocenylacetate ion at low pH to yield the dipolar ion.

Reaction (vi), on the other hand, may be readily conceived of as being reversed in acid solution. Another argument for its acceptance here is that when the solution containing the dipolar ion is made alkaline, the electronic spectrum changes quite appreciably in a way fully consistent with there ceasing to be a *ferricenium* group, but not compatible with there being a *ferrocenyl* group, in that there is no suggestion of an absorption band at or about 440 nm, which absorption is accepted as a universal characteristic of ferrocene and substituted ferrocenes. Authentic spectra of the cyclopentadienylcyclopentadieneiron system are not available for comparison.

However, since subsequent acidification does not cause a quantitative regeneration of the dipolar ion, it follows that one of the steps, either reaction (vi) on making alkaline or the reverse of reaction (vi) on acidifying, is not quantitative. For the latter, one may conceive of reaction (vii) as an alternative:



(vii)

Its occurrence would be consistent with the recovery of ferrocenylacetic acid after the decay of the dipolar ion. The other more polar compound obtained as a decomposition product may result from decarboxylation which could conceivably yield ferrocenylmethanol.

For ferrocenoate anion, the value of $k_1/k_2 = 1.4 \times 10^{-3}$ mol dm$^{-3}$ leads, assuming that $k_2 \leqslant 10^{10}$ dm$^3$ mol$^{-1}$ since it cannot exceed the diffusion controlled limit to $k_1 \leqslant 1.4 \times 10^7$ s$^{-1}$, which means that the lifetime of the photoexcited state, $(\mathrm{FcCO_2^-})^*$, $k_1^{-1} \geqslant 0.07$ μs. Since the transient absorptions seen in the region 400—800 nm on flashing solutions not containing $N_2O$ depend on the range of wavelengths of the exciting light in a different manner from the permanent absorption at 625 nm, it may be deduced that these transients are unrelated to the photoexcited state. In any case, one would not expect to detect the latter more than 100 μs after the onset of the flash unless its lifetime were considerably in excess of the minimum value deduced above.

When the excited precursor, $(\mathrm{FcCO_2^-})^*$, transfers an electron to $N_2O$, an absorption is detected at *ca.* 625 nm, part of which persists for at least a second; in view of this the visual observation that the blue colour fades would suggest that the initial product undergoes some further reaction. This initial product may well be the dipolar ion, $\overset{+}{\mathrm{Fc}}\mathrm{CO_2^-}$, but the identity of the further product presents something of an enigma since, although it is not extracted from the aqueous layer in acid solution and has an absorption maximum at 255 nm, it appears uncharacteristic of a ferricenium species, the decadic extinction coefficient of this peak being only *ca.* 330 $\mathrm{M^{-1}\,cm^{-1}}$ and not the more normal value of *ca.* $1.2 \times 10^4$ $\mathrm{M^{-1}\,cm^{-1}}$. However, it has been established that this further product can be reduced to ferrocenoic acid. Conceivably, the initial and the subsequent product may differ only in regard to the degree of interaction between the carboxylate group and the iron atom of the ferrocenyl group.

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