Redox Reactions of Organic Radicals with Ferrocene/Ferricenium Species in Aqueous Solution. Part 1. Radicals Derived from Carboxylic Acids

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An investigation is reported of the diminution of the photochemical yield of the carboxyalkylferricenium zwitterion from 4-ferrocenylbutanoate in aqueous solution at pH 9 containing N_2O, by the addition of small amounts of aliphatic acids. The extent is shown to depend both on the rate constant for the reaction with the anion of the hydroxyl radical generated from the photochemical process, and on the redox nature of the resulting radical anion. Both are reported for the anions of nine carboxylic acids, some of which have an hydroxy group in the α-position.

It has been shown previously[1,2] that carboxyalkylferrocenes may be photo-oxidised in aqueous solution by light of *ca.* 230–250 nm, in the presence of an electron acceptor such as N_2O, which is transparent at these wavelengths. Electron transfer from the photoexcited ferrocenyl group to N_2O leads[1,2] to the corresponding carboxyalkylferricenium dipolar ion, a molecule of N_2, and an OH radical. The radical then oxidises[3,4] another carboxyalkylferrocene to the corresponding ferricenium species.

In the presence of a low concentration of a species RH, with which the hydroxyl radical readily reacts by hydrogen-atom abstraction, there is a competing reaction for the OH radical. Its occurrence involves the formation of the radical $R^{\bullet}$ in the presence of, at least, an equivalent amount of carboxyalkylferricenium zwitterions. Possible consequences include the following: (I) If the radical $R^{\bullet}$ does not engage in any redox reactions with either the ferrocenyl anion or the ferricenium zwitterion, then the effect of added RH will be to decrease the quantum yield of the ferricenium species towards, in the limit, half its initial value.

(II) If $R^{\bullet}$ reacts with the ferricenium species and reduces it to its ferrocenyl analogue, then the addition of RH would diminish the quantum yield of the ferricenium species to an even greater extent. If all $R^{\bullet}$ species were to react in this way then, in the limit, the ferricenium quantum yield would tend to zero.

(III) If $R^{\bullet}$ were to oxidise the ferrocenyl species to the corresponding substituted ferricenium, then the presence of RH would have no apparent effect on the quantum yield of the ferricenium zwitterion.

It is of course possible that the radical $R^{\bullet}$ is by nature of type II or type III but that the relevant redox reaction does not occur quickly or quantitatively. It is then quite probable that the extent of reaction which does occur takes place over a longer interval of time so that a decrease or a growth in the concentration of the ferricenium species might be observable on the millisecond time scale or longer.

The above assertions about the effect of added RH on the ferricenium quantum yield implicitly assume that the species RH is transparent to the exciting light. For this reason, the use of aromatic compounds is ruled out since they absorb so strongly over the relevant wavelength range, even at very low concentrations.

More quantitatively, the initial photochemical events are summarised by reaction (1). In the absence of RH, this will be followed only by reaction (2), and so the quantum yield of the ferricenium zwitterion, $\varphi(\mathrm{F\overset{+}{c}})$ will be given by twice the primary quantum yield, *i.e.* $\varphi(\mathrm{F\overset{+}{c}})_0 = 2\varphi_p$.

$$\mathrm{Fc(CH_2)_\mathit{n}CO_2^-} + \mathrm{N_2O} + h\nu = \mathrm{F\overset{+}{c}(CH_2)_\mathit{n}CO_2^-} + \mathrm{N_2} + \mathrm{O^-}(\xrightarrow{H^+} \mathrm{OH}) \quad (1)$$

$$\mathrm{OH} + \mathrm{Fc(CH_2)_\mathit{n}CO_2^-} \longrightarrow \mathrm{F\overset{+}{c}(CH_2)_\mathit{n}CO_2^-} + \mathrm{OH^-} \quad (2)$$

In the presence of RH there is also the reaction (3). If the radical $R^{\bullet}$ is of type I then the consequence for the ferricenium quantum yield may be shown by equation (4) where, for convenience, the concentration of the carboxyalkylferrocene is represented by [Fc]. Rearranging, we obtain equation (5) which shows that the left hand side should be a linear function of the concentration of added RH.

$$\mathrm{OH} + \mathrm{RH} \longrightarrow \mathrm{H_2O} + \mathrm{R^{\bullet}} \quad (3)$$

$$\varphi(\mathrm{F\overset{+}{c}}) = \varphi_p\left\{1 + \frac{k_2[\mathrm{Fc}]}{k_2[\mathrm{Fc}] + k_3[\mathrm{RH}]}\right\} \quad (4)$$

$$\frac{1}{\varphi(\mathrm{F\overset{+}{c}} - \varphi_p)} = \frac{1}{\varphi_p}\left(1 + \frac{k_3[\mathrm{RH}]}{k_2[\mathrm{Fc}]}\right) \quad (5)$$

If the radical $R^{\bullet}$ is of type II and quantitatively reduces the ferricenium zwitterion, then the relevant equation is:

$$\begin{aligned}\varphi(\mathrm{F\overset{+}{c}}) &= \varphi_p\left(1 + \frac{k_2[\mathrm{FC}]}{k_2[\mathrm{Fc}] + k_3[\mathrm{RH}]} - \frac{k_3[\mathrm{RH}]}{k_2[\mathrm{Fc}] + k_3[\mathrm{RH}]}\right)\\ &= 2\varphi_p\left(\frac{k_2[\mathrm{Fc}]}{k_2k\mathrm{Fc}] + k_3[\mathrm{RH}]}\right) \quad (6)\end{aligned}$$

It follows that

$$\frac{1}{\varphi(\mathrm{F\overset{+}{c}})} = \frac{1}{2\varphi_p}\left(1 + \frac{k_3[\mathrm{RH}]}{k_2[\mathrm{Fc}]}\right) \quad (7)$$

in which the l.h.s. again shows a linear variation with RH concentration. From both of these plots, the ratio of slope/intercept leads to a value for the rate constant ratio, k_3/k_2.

Thus, a study of the quantitative effect of an added transparent solute RH on the quantum yield of the ferricenium species can lead both to information on the redox behaviour of the radical $R^{\bullet}$ towards the ferrocene/ferricenium species and also to an estimate of the rate constant for the reaction of the hydroxyl radical with RH.

The first group of compounds studied were carboxylic acids.

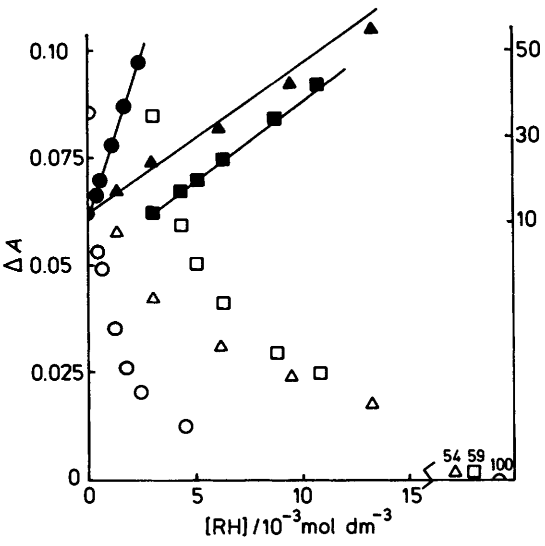

Figure 1. Absorbance change at 625 nm caused by a flash of 442 J as a function of the concentration of added formic acid (○), lactic acid (△), and glycolic acid (□) to 2.5×10^{-4} mol dm^{-3} 4-ferrocenylbutanoate in 0.03 mol dm^{-3} borax containing 0.023 mol dm^{-3} nitrous oxide. The filled symbols relate to the right-hand scale. The points for glycolic acid are displaced to the right for clarity. The absorbances are the constant values found after the flash for formic acid, 0.5 ms after for lactic acid and 3 ms after for glycolic acid.

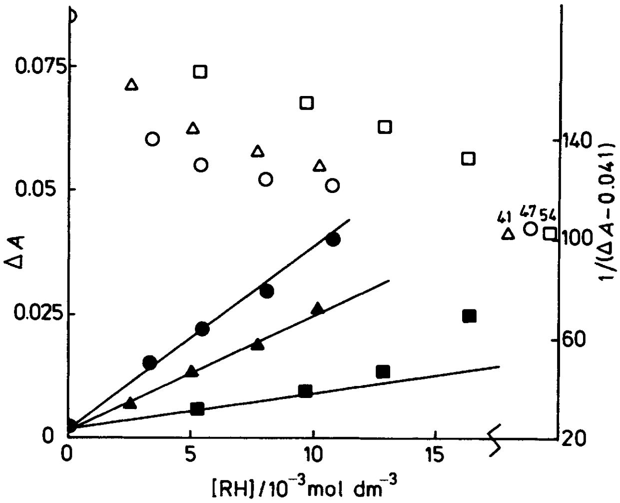

Figure 2. Absorbance change at 625 nm as a function of the concentration of added propionic acid (○), succinic acid (△), and malonic acid (□). The filled symbols relate to the right-hand scale. All absorbance values were those measured immediately after the flash.

While these are not strictly transparent at 230–250 nm, if acids containing an aromatic system are excluded, the extent of light absorption in solutions containing sufficient acid for reaction (3) to predominate over reaction (2) is quite slight, except in the case of a few species such as acetate ion with which the OH radical reacts slowly. Such compounds were therefore also excluded from the survey.

Experimental

4-Ferrocenylbutanoic acid was prepared as previously described.[1] Other chemicals were of AnalaR grade or, if this was not available, of the purest grade supplied. Doubly distilled water was used in the preparation of solutions and in the rinsing of apparatus. Solutions were made up in 0.03 mol dm^{-3} borax to maintain pH 9 and when the amount of acid being added to a sample was appreciable, an equivalent amount of KOH was added also. Since the ferrocenyl anion undergoes slow oxidation in these solutions, presumably from dissolved oxygen, solutions were freshly made up every few days.

After a sample had been degassed by four cycles of freeze–pump–thaw, it was equilibrated at 20 °C with N_2O at a pressure of 640 Torr to give a concentration[5] of 0.023 mol dm^{-3}. The cells and the flash photolysis apparatus have been previously described.[1,6] The concentric-filter compartment was filled with distilled water, the cell was put in position and the absorbance change at 625 nm immediately after the discharge of 442 J through the flash tubes was monitored.

Results

When formic acid was added to the system the absorbance change at 625 nm produced as a consequence of and during the flash diminished sharply as shown in Figure 1, and at moderate concentrations disappeared altogether. This indicates that the CO_2^- radical anion formed by the attack of the hydroxyl radical on formate ion is of type II and that the reaction (8)

$$CO_2^- + \overset{+}{Fc}(CH_2)_3CO_2^- \longrightarrow CO_2 + Fc(CH_2)_3CO_2^- \quad (8)$$

occurs with a high efficiency.

When propionic acid was added, at the end of the flash a less extensive decrease was seen, with a slight fall in absorbance over the next few milliseconds. Since the initial absorbance change, plotted in Figure 2, levels out at half the value in the absence of propionic acid, hydrogen-atom abstraction must lead to a radical with a negligible tendency to reduce the ferricenium species. It is known from e.s.r. studies that OH attack will lead[7,8] to the radicals $CH_3\dot{C}HCO_2^-$ and $\dot{C}_2H_2CH_2CO_2^-$, which should both be of type I.

With low concentrations of lactic acid, the absorbance at 625 nm remained constant after the flash, but at higher concentrations a slight decrease is observable over the next 0.5 ms. This final value, plotted in Figure 1, tends towards zero at higher concentrations, indicating that the radical anion, shown[9] to be $CH_3\dot{C}(OH)CO_2^-$, shows type II behaviour but that its reaction with the ferricenium zwitterion, reaction (9),

$$CH_3\dot{C}(OH)CO_2^- + \overset{+}{Fc}(CH_2)_3CO_2^- \longrightarrow CH_3COCO_2^- + H^+ + Fc(CH_2)_3CO_2^- \quad (9)$$

is slower than reaction (8).

The behaviour of glycolic acid was found to be similar, except that the decrease in absorbance following the flash was slightly greater and extended over a few milliseconds. The results, also shown in Figure 1, indicate that the radical anion, $\dot{C}H(OH)CO_2^-$ behaves similarly, with a slightly slower reaction.

When succinic acid is added to the system the absorbance change at 625 nm after the flash is decreased to half its initial value as shown in Figure 2. A slight fall in the absorbance was found over the next fraction of a second, showing that the radical dianion, $^-O_2CCH_2\dot{C}HCO_2^-$ has a slight tendency to reduce the ferricenium species.

The effect of malic acid was found to mirror that of lactic acid, with only a slight change in the absorbance seen for *ca.* 0.5 ms after the flash, and this final value approaching zero as the concentration is increased, as shown in Figure 3. This implies the occurrence of reaction (10).

$$^-O_2CCH_2\dot{C}(OH)CO_2^- + \overset{+}{Fc}(CH_2)_3CO_2^- \longrightarrow {}^-O_2CCH_2COCO_2^- + H^+ + Fc(CH_2)_3CO_2^- \quad (10)$$

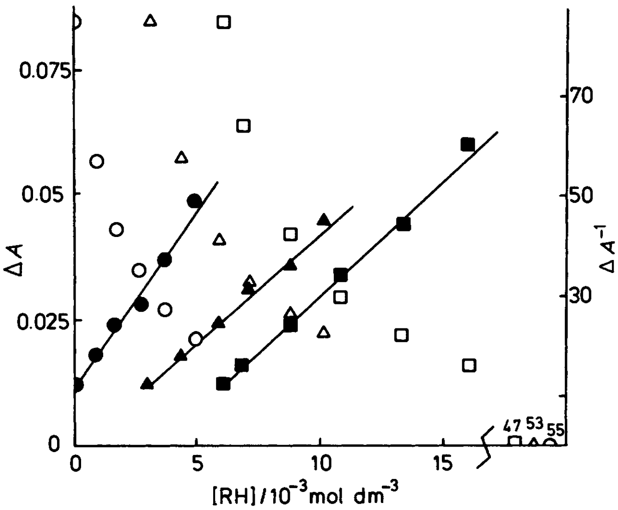

Figure 3. Absorbance change at 625 nm as a function of the concentration of added malic acid (○), tartaric acid (△) and displaced 3×10^{-3} mol dm^{-3} to the right and tartronic acid (□) and displaced 6×10^{-3} mol dm^{-3} to the right. The filled symbols relate to the right hand scale. The absorbances are the constant values found 0.5 ms after the flash for malic acid and 3 ms after the flash for tartaric and tartronic acids.

The consequences of the addition of tartaric acid are similar, but with the absorbance falling slightly over a few milliseconds. The final value, shown in Figure 3, tends to zero at higher concentrations so we deduce that the reaction of this radical dianion occurs slightly more slowly.

The addition of tartronic acid produces a very similar effect, with a slight fall in the absorbance over a few milliseconds to a value shown in Figure 3. This indicates the occurrence of reaction (11).

$$^{-}O_2C\dot{C}(OH)CO_2^- + F\overset{+}{c}(CH_2)_3CO_2^- \longrightarrow {}^{-}O_2CCOCO_2^- + H^+ + Fc(CH_2)_3CO_2^- \quad (11)$$

Addition of malonic acid to the system causes the absorbance change at 625 nm after the flash to decrease to just under half its original value as shown in Figure 2. This deviation from type I behaviour is attributed to light absorption by the solute at the fairly high concentrations required for it to scavenge the majority of hydroxyl radicals. However, over the following millisecond or so, an increase in absorbance was seen which implied that the radical dianion, $^{-}O_2C\dot{C}HCO_2^-$, could oxidise the ferrocenyl species, but considering how much higher the concentration of ferrocenyl is than that of ferricenium species, this reaction was rather inefficient. It was also found that the time scale for this oxidation depended on the amount of malonate present, in that it took place more quickly the higher the concentration, which suggests that this slow reaction is catalysed by the malonate ion.

Figures 1–3 also show the reciprocal plots appropriate to the redox behaviour of each radical. Equation (5) is tested in Figure 2 and equation (7) in Figures 1 and 3. The greatest deviations found were for malonate, in the expected direction regarding the factor mentioned above. From the gradient: intercept ratio, the relative rate constant k_3/k_2 was evaluated for each solute. Assuming, as seems reasonable,[3] that the rate constant for the reaction of the hydroxyl radical with 4-ferrocenylbutanoate anion will be much the same[4] as that with 3-ferrocenylpropanoate anion, namely 10.9×10^9 dm^3 mol^{-1} s^{-1}, the value of the rate constant k_3 is derived for each species, as shown in the Table.

In addition, experiments were carried out to test the effect of air in the solutions. For the system with no added RH but with N_2O present, allowing air into the vessel and equilibrating it with the solution, to produce an O_2 concentration of the order of 3×10^{-5} mol dm^{-3} had no effect. With RH also present it was found, in every case but one, that the absorbance at the end of the flash was essentially unchanged but that this value then increased over the following tens of milliseconds, consistent with the conversion of the radical R$^{\bullet}$ into $RO_2^{\bullet}$ which behaves as an oxidising species. With formate ion, the absorbance at the end of the flash was enhanced by the presence of O_2 and remained constant thereafter. This would be consistent with a more rapid reaction of CO_2^- with O_2, known to involve electron transfer and not addition [reaction (12)]. More recent

$$CO_2^- + O_2 \longrightarrow CO_2 + O_2^- \quad (12)$$

work has shown that O_2^- reduces the ferricenium zwitterion in a rather slow reaction, not apparent on the millisecond time scale.

Discussion

One of the notable features of these results is the finding that when the radical anion CO_2^- is formed in the presence of an equimolar quantity of the ferricenium zwitterion, these two species react together quite efficiently, even though the rate constant for the combination of two CO_2^- radicals is itself quite high,[10] with $2k = 1.2 \times 10^9$ dm^3 mol^{-1} s^{-1} at this pH and ionic strength.

The reason is not, apparently, that the combination process is inconsequential, for it has been found[11] that oxalate does not reduce the ferricenium zwitterion. More probably it is because each $CO_2^{-\bullet}$ radical ion is necessarily formed in the vicinity of a ferricenium species, so that the reduction process is virtually an in-cage reaction. If the reaction were genuinely homogeneous, the fact that no decay of ferricenium species is seen after the fall-off of the scattered light from the flash makes observation possible, at approximately 70 μs after the commencement, must imply an impossibly high rate constant for reaction (8) given the smallness of the concentrations.

At very low formate concentrations it would no longer be expected that each $CO_2^{-\bullet}$ radical is formed beside a ferricenium species, but under these conditions where only a fraction of the hydroxyl radicals are scavenged by formate, the concentration of ferricenium species formed from reactions (1) and (2) is much greater than that of $CO_2^{-\bullet}$ and so the redox reaction would readily predominate over combination of $CO_2^{-\bullet}$ with itself.

With all the other radicals of type II a change in the absorbance at 625 nm was observed on the time scale of *ca.* 1 ms, indicating that these radical anions react with the ferricenium species more slowly than does $CO_2^{-\bullet}$, but given the low concentrations this does not imply that the reactions are extremely slow. Their mode of reaction is apparently similar to that[12] of the radical $CH_3\dot{C}HOH$, but in the present work the reduction process occurs with greater efficiency, which can only be attributed to the proximity of the carboxylate.

Of the nine anions used in this work, formate is the only one on which several previous measurements of the rate constant for OH attack had been made. The value in the Table lies well within the range of previous determinations and is close to the recommended value.[13] The present values for propionate and glycolate show good agreement with previous work but in all other cases the only rate constant determination listed[13] lies well outside the limits of the present work. Our value for succinate, which exceeds the previous estimate, is closer to that for propionate. That for malonate is much less than was found

Table. Rate constants for reaction of OH with anions.

Anion, RH	$k(\mathrm{OH} + \mathrm{RH})/10^8\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$
HCO_2^-	36 ± 3
$CH_3CH_2CO_2^-$	8.7 ± 0.8
$^-O_2CCH_2CH_2CO_2^-$	5.3 ± 0.5
$^-O_2CCH_2CO_2^-$	1.7 ± 0.2
$CH_2(OH)CO_2^-$	8.7 ± 0.7
$CH_3CH(OH)CO_2^-$	8.2 ± 0.8
$^-O_2CCH_2CH(OH)CO_2^-$	16.4 ± 1.3
$^-O_2CCH(OH)CH(OH)CO_2^-$	10.1 ± 0.8
$^-O_2CCH(OH)CO_2^-$	10.7 ± 1.0

before and the present value seems reasonable in view of the known effect of the carboxylate group on reactivity.

For the other hydroxy acids the present values are all higher: that for lactate is much greater and, given the agreed value for propionate and the known effect of the hydroxy group in assisting H atom abstraction, it would seem a more probable value. That for malate is nearly twice the previous value [13] and its comparison with the value for succinate attests to the effect of the hydroxy substituent. It also exceeds our value for tartrate which suggests that the presence of another hydroxy group at the α-position is a hindrance to hydrogen-atom abstraction. Comparison of the values listed [13] for propan-1-ol ($2.8 \times 10^9\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$), propane-1,2-diol ($1.7 \times 10^9\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$) and propane-1,3-diol ($2.5 \times 10^9\ \mathrm{dm^3\ mol^{-1}}$) would tend to support this.

No previous determination is listed [13] for tartronate, which, as expected, was found to be much more reactive than malonate.

References

1 E. K. Heaney and S. R. Logan, *J. Chem. Soc., Perkin Trans. 2*, 1977, 1353.

2 E. K. Heaney and S. R. Logan, *J. Chem. Soc., Perkin Trans. 2*, 1978, 590.

3 S. R. Logan and G. A. Salmon, *J. Chem. Soc., Perkin Trans. 2*, 1983, 1781.

4 S. R. Logan and G. A. Salmon, *Radiat. Phys. Chem.*, 1984, **24**, 593.

5 E. Janata and R. H. Schuler, *J. Phys. Chem.*, 1982, **86**, 2078.

6 E. K. Heaney, S. R. Logan, and J. A. Powell, *J. Chem. Soc., Faraday Trans. 1*, 1977, **73**, 669.

7 H. Paul and H. Fischer, *Z. Naturforsch., Teil A*, 1970, **25**, 443.

8 F. R. Hewgill and G. M. Proudfoot, *Aust. J. Chem.*, 1976, **29**, 637.

9 W. T. Dixon, R. O. C. Norman, and A. L. Buley, *J. Chem. Soc.*, 1964, 3625.

10 G. V. Buxton and R. M. Sellars, *J. Chem. Soc., Faraday Trans. 1*, 1973, **69**, 555.

11 S. R. Logan, unpublished work.

12 W. P. Armstrong and S. R. Logan, *J. Photochem.*, 1983, **22**, 157.

13 G. V. Buxton, C. L. Greenstock, W. P. Helman, and A. B. Ross, *J. Phys. Chem. Ref. Data*, 1988, **17**, 513.

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