THE ROLE OF ALIPHATIC ALCOHOLS IN INHIBITING THE PHOTO-OXIDATION OF FERROCENYL-SUBSTITUTED CARBOXYLIC ACIDS

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Summary

It is shown that the scheme proposed earlier for the mechanism of inhibition of the photo-oxidation of ferrocenyl-substituted carboxylic acids ($Fc(CH_2)_nCO_2H$) is incorrect. Instead it is suggested that the role of an alcohol in this system is that of a scavenger for the hydroxyl radicals resulting from the photochemically initiated electron transfer to N_2O, thus preventing the OH radicals from oxidizing a further anion to the ferricenium zwitterion. The experimental data are shown to be quantitatively consistent with this mechanism and the rate constant for the reaction of OH with the anion $Fc(CH_2)_nCO_2^-$ is estimated to be in excess of $10^{10} M^{-1} s^{-1}$.
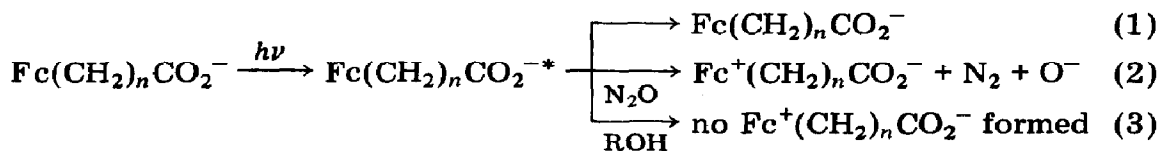
1. Introduction

Previous photochemical studies [1 - 3] have shown that in the photo-oxidation of carboxyalkylferrocenes ($Fc(CH_2)_nCO_2^-$ ($n = 1, 2, 3$ or 4)) in aqueous solution in the presence of N_2O molecular nitrogen is produced along with the carboxyalkylferricenium dipolar ion. Thus the first part of the photochemical reaction can be described by the stoichiometric equation

$$Fc(CH_2)_nCO_2^- + N_2O + h\nu = Fc^+(CH_2)_nCO_2^- + N_2 + O^- \qquad (I)$$
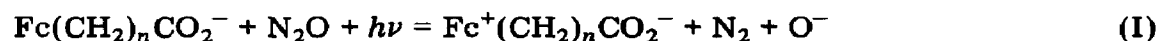
Since flash photolysis studies of deaerated solutions showed no indications of a transient absorption attributable to the solvated electron [4], it was concluded [1, 2] that the mechanism of the above process involves an electron transfer to N_2O from the photoexcited state resulting from the absorption of the light quantum. Also, it was observed [2, 3] that the yield of the ferricenium species decreased significantly on the addition of a small amount of an aliphatic alcohol. In this process ethanol was the most efficient and *tert*-butanol the least efficient of the common alcohols used, and methanol-d_4 was less efficient than methanol by a factor of 2.0.

This effect of alcohols appeared to be due to some inhibitory mechanism by which ROH prevented the photoexcited state formed in the initial

process from transferring an electron to N_2O. The scheme proposed was as follows:

$$Fc(CH_2)_nCO_2^- \xrightarrow{h\nu} Fc(CH_2)_nCO_2^{-*} \begin{cases} \longrightarrow Fc(CH_2)_nCO_2^- & (1) \\ \xrightarrow{N_2O} Fc^+(CH_2)_nCO_2^- + N_2 + O^- & (2) \\ \xrightarrow{ROH} \text{no } Fc^+(CH_2)_nCO_2^- \text{ formed} & (3) \end{cases}$$

The resulting equation

$$\frac{1}{\phi(Fc^+(CH_2)_nCO_2^-)} = \frac{1}{\phi(Fc(CH_2)_nCO_2^{-*})}\left(1 + \frac{k_1 + k_3[ROH]}{k_2[N_2O]}\right) \tag{4}$$

was tested and the experimental data were found to be consistent with the mechanism by showing [2, 3] that at constant N_2O concentration the reciprocal of the absorbance change due to the product zwitterion is a linear function of the ROH concentration.

It was desired to investigate further the interference of aliphatic alcohols with this photo-oxidation process and to subject the above scheme to more exhaustive tests with a view to clarifying the exact mechanism involved. It was hoped that such studies would explain the observed differences, including the H−D isotope effects, in the efficiency of the various alcohols in inhibiting this photo-oxidation.

2. Experimental details

3-ferrocenylpropanoic acid was prepared as previously described [2]. Solutions were made up using doubly distilled water and all other solutes were of AnalaR grade.

Apart from the experiments summarized in Table 1, the solutions were degassed by applying five freeze−pump−thaw cycles. When it was desired to measure nitrogen yields, the permanent gases were collected using a Töpler pump [5]. Steady illumination experiments were carried out using a low pressure mercury lamp with a filter of 2 cm of distilled water interposed to remove the 185 nm line. The intensity of the 254 nm light from the mercury lamp was measured *in situ* by ferrioxalate actinometry [6] using the procedures already detailed [5]. The flash photolysis sytem was used as previously described [7].

In the experiments reported in Table 1, the cells used were fitted with a finger sufficiently large to contain the sample over which a septum cap was fitted. Degassing and saturation with N_2O were achieved simultaneously by bubbling N_2O through the solution in this finger using appropriate syringe needles. Other solutes were then added subsequently, except in the case of solids where this was not practicable and where the loss of solute during N_2O bubbling was less likely because of the lower volatility.

3. Results and discussion

In the previous work [1, 2] with carboxyethylferrocene ($Fc(CH_2)_2CO_2^-$) (I) solutions were made up in borax buffer. This was a convenient way of achieving a slightly alkaline medium in which the parent acid could readily be dissolved, and it was shown [2] that the photo-oxidation process was unaffected if a similar pH was obtained without borax. It was thought desirable to investigate explicitly whether the inhibition produced by the added alcohol depended in any way on the buffer.

A solution of I at a concentration of 2.5×10^{-4} M was made up to a pH of 9.3 using dilute aqueous KOH. The absorbance increase at 625 nm was measured by flashing a deaerated N_2O-saturated sample. When 10^{-1} M ethanol was added the absorbance was reduced to 2%, and when 10^{-1} M methanol was added it was reduced to 6%, thus clearly showing that the inhibition effect did not depend on the presence of borax.

A 2.5×10^{-4} M solution of I made up with 10^{-2} M borax was used to perform a series of experiments in which measured amounts of either ethanol or ethanol-d_6 were added. These results are reported in Fig. 1, which also demonstrates the existence of an H–D isotope effect of a magnitude comparable with that previously reported [2] for methanol. The ethanol-d_6 curve can be regarded as a sideways displacement of that for undeuterated ethanol, with the inhibitory effect of the former being less by a factor of 1.6.

As a further test of the mechanism proposed for the inhibition process, a series of experiments in which the N_2O concentration was varied while that of ethanol was kept constant was carried out to complement the experiments already performed [2] in which the ethanol concentration was varied while that of N_2O was kept constant. From the postulated mechanism, the reciprocal of the absorbance change should be a linear function of reciprocal N_2O concentration. The data satisfy this requirement, as shown in Fig. 2.
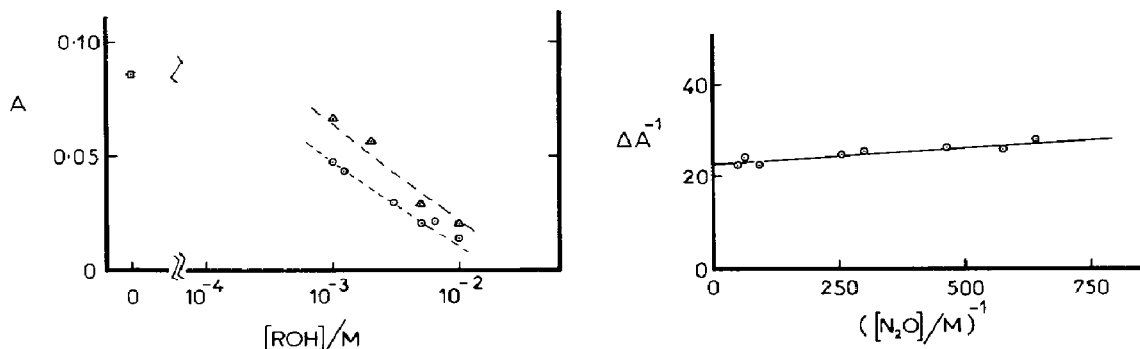

Fig. 1. Plots of the absorbance change at 625 nm against the alcohol concentration from a series of experiments using solutions containing 2.5×10^{-4} M I, 10^{-2} M borax and 1.2×10^{-2} M N_2O (flash energy, 442 J): $\odot$, ethanol; $\triangle$, ethanol-d_6.

Fig. 2. Plots of the reciprocal of the absorbance change at 625 nm against the reciprocal of the N_2O concentration for a series of experiments using solutions containing 2.5×10^{-4} M I, 10^{-2} M borax and 1.2×10^{-3} M ethanol (flash energy, 442 J).

However, the intercept on this graph, which on the basis of eqn. (4) can be equated to $\{\phi(\mathrm{Fc(CH_2)}_n\mathrm{CO_2}^{-*})\}^{-1}$, was found to be 22.7 for 1.2×10^{-3} M ethanol, whereas a value of 10.7 was expected on the basis of the previous experiments [2] with no ethanol present but with all other experimental parameters identical. Furthermore, the ratio of slope to intercept is, from eqn. (4), equal to $(k_1 + k_3[\mathrm{ROH}])/k_2$. The data in Fig. 2 yield a value of 2.9×10^{-4} M for the slope-to-intercept ratio, whereas the value expected from the previously determined [2] ratios for k_1/k_2 and k_3/k_2 was 6.9×10^{-3} M.

It would follow from these inconsistencies, which are of a magnitude that cannot be attributable to experimental error, that the mechanism on which eqn. (4) is based cannot be completely correct. In particular, the yield of the ferricenium zwitterion in the presence of a constant ethanol concentration is found to vary with the N_2O concentration by far less than would be required if the role of alcohols in the inhibition process was of the nature envisaged in this scheme. The magnitude of this discrepancy must suggest that N_2O and ROH do not in fact compete for the same species.

An alternative approach is to investigate the effect of added ethanol on the quantum yield of nitrogen. This is less easy to achieve in that the measurement of gas yields is more painstaking and inherently less precise than that of absorbance changes. However, the amount of nitrogen produced should serve as a very good measure of the extent of electron transfer to N_2O, whereas an absorbance increase at 625 nm may be due in part to a species other than the ferricenium dipolar ion and in any case part of the yield of the latter may result from the oxidation of I by the hydroxyl radical resulting from electron transfer to N_2O.

Samples of an aqueous solution containing 5×10^{-4} M I, 10^{-2} M borax and a known amount of ethanol were degassed and N_2O was added to a concentration of 0.02 M. Each sample was then illuminated with 254 nm radiation in precisely the same way and for the same period of time while in a thermostat at 25 °C. It was found that the nitrogen yield increased steadily as the concentration of ethanol was increased, as shown in Fig. 3, and that
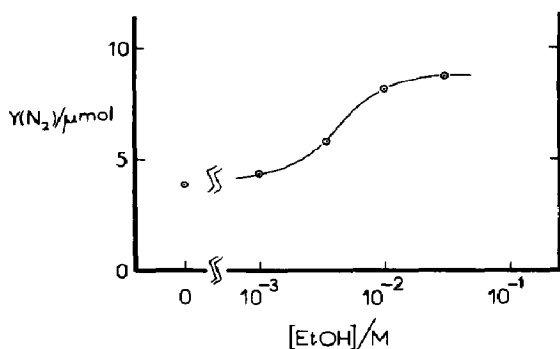

Fig. 3. The dependence of the yield of nitrogen on the ethanol concentration when a solution containing 5×10^{-4} M I, 10^{-2} M borax and 2×10^{-2} M N_2O is irradiated with 254 nm light at 25 °C for a constant period of time (20 min).

an increase of a factor of 2.3 was attained in the sample containing 3×10^{-2} M ethanol.

The most significant aspect of this result is that such an increase in the ethanol concentration does not bring about a decrease in the yield of nitrogen. This can only mean that ethanol does not to any appreciable extent inhibit the processes summarized in eqn. (I). Thus its interference with the photo-oxidation must arise from some event subsequent to the electron transfer to N_2O. The observed increase in the nitrogen yield does not represent an increase in the quantum yield of eqn. (I) in terms of the number of molecules of product formed per quantum absorbed by I. When no ethanol is present and the ferricenium dipolar ion is readily formed, the latter, since it has a most intense absorption band at 255 nm [1, 2], diminishes (by the inner filter effect) the fraction of the incident 254 nm light absorbed by I. Thus under these conditions it is not possible to measure $\phi(N_2)$ accurately since it is exceedingly difficult to make a reliable correction for the fraction of incident light absorbed by this product. (In theory it should be possible to do so if an efficient internal stirrer were used [8], but the presence of such a device tends to increase the uncertainties in the gas yield.) However, with sufficient ethanol present to minimize the build-up of the ferricenium dipolar ion, the quantum yield should be given by the ratio of nitrogen molecules produced to the number of 254 nm quanta absorbed in the cell, and at an ethanol concentration of 3×10^{-2} M the value obtained was 0.11.

A few experiments were performed to test whether substances other than simple alcohols could also inhibit the photo-oxidation of I to the ferricenium dipolar ion. Samples of a solution containing 2.5×10^{-4} M I and saturated with N_2O were prepared and various organic solutes were added at concentrations of 10^{-2} M. The absorbance change at 625 nm produced by a flash of constant energy was then measured, and the ratios of such changes to that found with no additive present are listed in Table 1. These results indicate that the inhibition phenomenon is quite general.

It thus seems probable that the effect of organic compounds such as aliphatic alcohols in reducing the extent of photo-oxidation of the anion I to the dipolar ion is due, not to any interference with the initial photochemical process, but to the potential role of such compounds as scavengers for the hydroxyl radicals produced as a consequence of reaction (I). If, in the absence of such a solute, reaction (I) is followed by the reaction

$$OH + Fc(CH_2)_n CO_2^- \rightarrow OH^- + Fc^+(CH_2)_n CO_2^- \qquad (5)$$
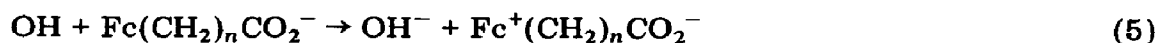
then the yield of the dipolar ion must inevitably be decreased by the presence of a solute such as ethanol when the reaction

$$OH + CH_3CH_2OH \rightarrow H_2O + CH_3\overset{\cdot}{C}HOH \qquad (6)$$

is expected to compete with reaction (5).

On this basis the extent of such a decrease would be expected to approach 50% as the concentration of ethanol is increased to the point

TABLE 1

Effect of addition of various organic solutes at 10^{-2} M on the absorbance change A at 625 nm produced in a solution containing 2.5×10^{-4} M 3-ferrocenylpropanoate ion and 10^{-2} M borax and saturated with N_2O (flash energy, 442 J)

Solute	A_s/A_0
Acetamide	0.60
Acetic acid	0.90
Acetone	0.06
Acetonitrile	0.93
Benzene	0.67
Chloroform	0.60
Diethyl ether	0.84
Ethyl acetate	0.80
Ethylene glycol	0.73
Formic acid	0.16
Glycine	0.28
Methanol	0.30
n-propanol	0.41
Trichloroacetic acid	0.57

A_s, A in the presence of 10^{-2} M solute; A_0, A with no solute present.

where reaction (6) predominates over reaction (5). The fact that the decrease frequently exceeds this figure may well be attributable to further reactions of the radical (mostly $CH_3\dot{C}HOH$ in the case of ethanol) produced by the attack of the OH radical on the solute.

Considering the competition between the anion I and the added solute for the OH radicals produced from process (I), we obtain for the contribution to the quantum yield of the dipolar ion resulting from reaction (5) (as distinct from that produced in process (I)) the equation

$$\Delta\phi(Fc^+(CH_2)_nCO_2^-) = \phi(OH)\frac{k_5[I]}{k_5[I] + k_6[ROH]} \tag{7}$$

If we further assume, as seems to be the case, that virtually every radical species (such as $CH_3\dot{C}HOH$) generated in the scavenging of OH radicals can reduce or otherwise destroy one ferricenium dipolar ion, then the final quantum yield of the latter should be

$$\phi(Fc^+(CH_2)_nCO_2^-) \approx 2\phi(OH)\frac{k_5[I]}{k_5[I] + k_6[ROH]} \tag{8}$$

If we further assume [1, 2] that the mechanism by which process (I) is achieved involves the competition of reactions (1) and (2), then we have

$$\phi(N_2) = \phi(OH) = \phi(Fc(CH_2)_nCO_2^{-*}) \frac{k_2[N_2O]}{k_1 + k_2[N_2O]} \qquad (9)$$

Substituting this in eqn. (8) and writing I* for the photoexcited state from which electron transfer may occur to N_2O, we obtain

$$\phi(Fc^+(CH_2)_nCO_2^-) \approx 2\phi(I^*) \frac{k_2[N_2O]}{k_1 + k_2[N_2O]} \frac{k_5[I]}{k_5[I] + k_6[ROH]} \qquad (10)$$

This leads to the relation

$$\{\phi(Fc^+(CH_2)_nCO_2^-)\}^{-1} \approx \{2\phi(I^*)\}^{-1}\left(1 + \frac{k_1}{k_2[N_2O]}\right)\left(1 + \frac{k_6[ROH]}{k_5[I]}\right) \qquad (11)$$

which, like eqn. (2), would also predict a linear relationship between the reciprocal of the absorbance change and the alcohol concentration at a constant N_2O concentration. Thus the data in Fig. 1 and in similar earlier work using methanol [2, 3] are as readily accommodated by the present explanation as by the scheme proposed earlier [2] and summarized just before eqn. (4). The relative rate constants $k(OH + CH_3OH)/k(OH + CD_3OH)$ and $k(OH + C_2H_5OH)/k(OH + C_2D_5OH)$ have been determined [9] as 2.0 and 1.6 respectively, in excellent agreement with the isotope effects reported earlier [2, 3, 10] and in the present work.

The quantitative success of eqn. (11) with regard to the isotope effects prompts its application to estimate the rate constant of reaction (5). For a plot of reciprocal absorbance change against alcohol concentration the ratio of the slope to the intercept should be given by $k_6/k_5[I]$. When the values [9] of 8.6×10^8 M^{-1} s^{-1} and 1.85×10^9 M^{-1} s^{-1} are used for the rate constants $k(OH + CH_3OH)$ and $k(OH + C_2H_5OH)$ respectively, the data in Fig. 3 of the earlier work [2] and in Fig. 1 of the present work both lead to a value of 1.3×10^{10} M^{-1} s^{-1} for the rate constant for the reaction of OH with the I anion. When the first datum along with the ratio of slope to intercept of Fig. 2 of ref. 3 are used a value of 1.1×10^{10} M^{-1} s^{-1} is obtained for the rate constant of OH with the ferrocenylacetate anion. Similarly, from ref. 10, Fig. 1, we obtain a value of 7.8×10^9 M^{-1} s^{-1} for the rate constant of OH with the 4-(β[3]ferrocenophanyl)butanoate anion. High precision is not claimed for these values in view of the approximations involved in deriving eqn. (8), but their order of magnitude supports the claim that in such systems the hydroxyl radical readily oxidizes the ferrocenyl-substituted anion to the corresponding ferricenium dipolar ion. This is in accord with the results of recent pulse radiolysis studies [11].

Acknowledgments

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