

Journal of Organometallic Chemistry, 153 (1978) 229-237
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PHOTO-OXIDATION OF UNSATURATED FERROCENYL-SUBSTITUTED
 CARBOXYLIC ACIDS

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(Received March 6th, 1978)

Summary

In aqueous solution (pH 9) containing N_2O , the unsaturated acids trans- $FcCH=CH(CH_2)_nCO_2H$ ($n = 0$ and 1) and $FcC\equiv CCO_2H$ each undergo photo-oxidation, upon illumination with u.v. light of wavelength 240-250 nm, giving dipolar ferricenium species which may be chemically reduced back to the original acids. The mechanism of photo-oxidation, which is inhibited by ethanol, appears to be similar to that previously proposed for saturated ω -ferrocenylalkanoic acids.

Previous studies [1-3] of the photochemistry of ω -ferrocenylalkanoate anions $Fc(CH_2)_nCO_2^-$ ($n = 0-4$) have demonstrated that an electron may be readily transferred from a photo-excited state, presumably a triplet, whose lifetime exceeds 1 μs . As product, one obtains the corresponding dipolar ions $Fc^+(CH_2)_nCO_2^-$ which show considerable stability when $n \geq 2$.

For such systems where $n = 1-4$, the ferrocenyl and carboxylate groups are separated by an alkyl chain which insulates the groups from direct electronic interaction but

whose conformational flexibility allows the carboxylate group to attain a range of positions relative to the metal atom, including those of close approach. In order to assess the importance or otherwise of these factors in the photo-oxidation reaction, an investigation has been carried out of the behaviour of substrates for which the ferrocenyl and carboxylate groups are separated by a carbon-carbon multiple bond [*viz.* trans-FcCH=CHCO₂H (I) and FcC≡CCO₂H (II)] which introduces π-conjugation of the groups while simultaneously preventing their close intramolecular approach. A study has also been made of the properties of trans-FcCH=CHCH₂CO₂H (III) for which neither conjugation nor close approach of the terminal groups obtains.

The ferrocenyl-substituted acrylic (I) and propiolic (II) acids were synthesised by literature methods and the butenoic acid (III) was obtained by base-induced hydrolysis of its known methyl ester (see Experimental).

RESULTS AND DISCUSSION

trans-3-Ferrocenypropenoic acid (I)

When a solution of the acid (I) in aqueous borax buffer solution (pH 9) containing N₂O was illuminated by 254 nm radiation, N₂ was produced with a quantum yield, in the unstirred solution, of ca. 0.02, but there was very little change in the electronic spectrum over 220-700 nm.

Flash-photolysis studies of degassed solutions of (I) in aqueous borax buffer indicated that small transient absorptions, lasting a few milliseconds, were seen immediately after the flash, over the range 500-700 nm. Using very dilute solutions of (I), so that a 20 cm path length was sufficiently transparent to the analysing light in the near u.v., it was possible to

show that absorptions of similar duration and of greater magnitude occurred over the range 320-500 nm, with a maximum absorption at ca. 330 nm and a smaller peak at ca. 400 nm.

Using similar sets of solutions with N_2O added, absorptions were also found at the same wavelength ranges. These comprised both a transient part, lasting a few milliseconds and of comparable magnitude to that seen in the absence of N_2O , and a persisting element, present for at least a second, of magnitude approximately one-third of the total absorption detected at 100 μs after the onset of the flash. Like the transient portion, the persistent part also showed maxima at, ca. 330 nm and 400 nm.

These experiments led to the conclusions that (a) photo-oxidation of the anion was taking place in the presence of N_2O and that (b) as for the other acids studied previously [1-3], the mechanism did not involve photo-ejection, since the flash photolysis of degassed solutions yielded no indication of the presence of the solvated electron. Thus it is very likely that the photo-oxidation occurred by electron transfer to N_2O from a photo-excited state of the acid, in a manner analogous to that postulated previously [1-3].

To isolate the possibly numerous products of the u.v. irradiation of (I) under these conditions, a stirred 10^{-2} M aqueous solution in borax buffer containing N_2O was irradiated with light of 254 nm for 24 hours. Firstly, it was then extracted (still at pH 9) with dichloromethane to remove any non-polar products. This gave a pale yellow extract, but t.l.c. analysis showed that it contained only the acid (I). To remove the remainder of the unused acid, the solution was acidified and again extracted three times with dichloromethane. This left a pale green solution, whose electronic spectrum showed very weak absorption throughout the visible region up

to 680 nm, but an intense peak at 255 nm with a shoulder at 295 nm. When titanium(III) chloride was added to the acid solution, it became pale pink. Extraction with dichloromethane now produced a red organic layer which was shown to contain an acid, identified as (I) by t.l.c. By comparing the spectrum of the final product in a known volume of aqueous borax with that of a solution of known concentration, it was calculated, assuming quantitative reduction by titanium(III) chloride, that the decadic extinction coefficient of the dipolar ion at 255 nm was $3.45 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, which is considerably more than the value of $1.2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ reported [4] for the ferricenium ion at 250 nm.

Further flash-photolysis experiments were conducted in which the filter compartment of the cell was filled with solutions other than distilled water. For degassed solutions of (I), the use of the 15% aqueous acetic acid solution caused a considerable decrease in the transient absorption at 330 nm, but had little effect on that at 400 nm. A filter solution of $5 \times 10^{-3} \text{ M}$ aqueous benzoic acid resulted in no absorption being detected at 330 nm, but a decreased transient absorption was seen at 400 nm. Thus it may be concluded that these transients are not, or not entirely, attributable to the same species and that the species absorbing at 400 nm, but not that absorbing at 330 nm, may be generated by light of wavelength greater than 290 nm.

Using solutions containing N_2O , the results were found to be very similar in regard to the transient part of the absorption, but with the benzoic acid filter, no persistent absorption was seen at either wavelength and only a very small persistent absorption at 330 nm was found using the acetic acid filter. Thus the persistent absorptions produced

in the presence of N_2O may, unlike the transient absorptions, be due to a single species.

Further flash-photolysis experiments showed that the addition of 10^{-1} M ethanol to the buffered aqueous solutions had no effect on the transient absorptions, either in the absence or presence of N_2O . However, the presence of ethanol was found to eliminate the permanent absorptions otherwise seen when N_2O was added.

In summary, these experiments show that the excitation of the anion of (I) with u.v. light produces two transient species, visible for a few milliseconds and unaffected by N_2O or by ethanol. One requires light of wavelength less than 245 nm but the other can be produced by light of wavelength greater than 290 nm, which probably means that excitation within the absorption band centred at 294 nm is effective. Neither of these species is capable of the electron-transfer to N_2O , as shown by their detection with ethanol present, under which conditions no photo-oxidation is found to occur. In any case, one would expect, by analogy with the previous work [1-3], that the species which engages in electron-transfer with N_2O would have a lifetime of only a few microseconds, thus ruling out these entities with millisecond lifetimes.

It is difficult to be categorical as to whether there is any change after 1 second in the absorption produced on flashing in the presence of N_2O . It is not clear that the magnitude of the persistent absorptions seen by flash photolysis corresponds exactly with the absorbance of the ionic oxidation product in the visible region, but both seem attributable to the ferricenium dipolar ion, $F^+CCH=CHCO_2^-$.

trans-4-Ferrocenylbut-3-enoic acid (III)

A solution of (III) in 10^{-2} M borax buffer was degassed and, after addition of N_2O , was illuminated with 254 nm radiation with continual stirring. The yield of N_2 was collected and it was calculated that $\phi(N_2) \approx 0.02$. After acidification and extraction of the unused acid, a green aqueous layer was obtained whose electronic spectrum showed an intense peak at 255 nm and a weak absorption at 600-700 nm. This ionic compound was readily reduced to the original acid and so was taken to be the corresponding ferricenium species.

By flash-photolysis studies, using degassed solutions of (III) in aqueous borax buffer, only very slight transient absorptions were detected in the visible region. When N_2O was added, small persistent absorptions were found over the range 550 to 800 nm, but with no definite maximum. These absorptions were not seen when light of wavelength less than 290 nm was filtered out of the light from the flash using 5×10^{-3} M aqueous benzoic acid in the filter compartment and were reduced in intensity by about half when 15% aqueous acetic acid was used. Also, they were very appreciably diminished by the addition of 10^{-1} M ethanol.

For analogous reasons, a mechanism similar to that proposed for the acrylic acid (I) would appear to be operative in this case also. Since the persistent absorptions were rather small, probably through a combination of a rather small quantum yield and a low extinction coefficient, it was not considered feasible to elucidate details of the kinetic processes involved by finding how their magnitude depended on certain variable experimental parameters.

Ferrocenylpropynoic acid (II)

Similar experiments with aqueous solutions of (II) gave a quantum yield of N_2 of approx. 0.005 and the pale green solution of the ferricenium compound was found to have broad absorption peaks at 260 and 290 nm, but very little absorption over the range 550-700 nm.

When degassed solutions were flashed, a transient absorption was detected at 425 nm, with a lifetime of just less than 1 millisecond. With N_2O present, very small persistent absorptions were detected over the range 450-700 nm.

Thus it has been demonstrated that the anions of all three acids undergo photo-oxidation in a manner analogous to those of the fully saturated acids, $Fc(CH_2)_nCO_2^-$. In all cases, accurate quantum-yield measurements are difficult to obtain since one of the products absorbs strongly at the wavelength of excitation, but it appears that the quantum yields are appreciably less for these acids with unsaturated side-chains. Also, the ferricenium species obtained as the product of oxidation have much smaller absorptions in the visible region than had those [1-3] from the saturated acids. In all three cases, the mechanism must involve electron-transfer to N_2O rather than photo-ejection since, in the absence of N_2O , no intense transient is seen at around 700 nm attributable to the solvated electron. As in the case of the acids with saturated side-chains, photo-oxidation is inhibited by ethanol, but the elucidation of further details of the process is precluded because of the difficulty in monitoring the yields of products obtained in flash-photolysis experiments, on account of the low quantum yields and low extinction coefficients.

EXPERIMENTAL

Preparation of acids

3-Ferrocenylpropenoic acid (I) [5] and ferrocenylpropynoic acid (II) [6] were synthesised from formyl- and ethynyl-ferrocene respectively by literature methods. 4-Ferrocenylbut-3-enoic acid (III) was obtained by conventional base-induced hydrolysis of methyl trans-4-ferrocenylbut-3-enoate whose preparation has been reported [7] previously. The magnitudes of the vinylic coupling constants (ca. 16 Hz) in the ^1H n.m.r. spectra (CDCl_3 solutions) of the alkenoic acids (I) and (III) established that each compound contained a trans-substituted double bond.

Photochemical procedures

Triply-distilled water was used in all work and all apparatus was cleaned with Decon and carefully rinsed. The nitrous oxide was purified by trap-to-trap distillation and was degassed immediately before use. Other chemicals were of AnalaR grade.

The flash-photolysis apparatus has been previously described [8]. For steady illumination, a low-pressure mercury lamp was used with the interposition of 2 cm of distilled water to filter out the 185 nm line from the main resonance line at 254 nm.

Acknowledgements

Support of this work by the Science Research Council is gratefully acknowledged.

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