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Photoinduced Reactions of Ferrocenium Ion in Acetonitrile–Alcohol Solution

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Abstract

The photoinduced reactions of ferrocenium ion in acetonitrile are described in the presence of benzylalcohol, benzhydrol or propanol-1. The alcohol oxidation into carbonyl compound and the photoreduction or photodecomposition of ferrocenium are observed in the case of benzylalcohol. A photocatalysed alcohol dehydration to the ether oxide is observed in the case of benzhydrol. It is shown that the LMCT transition excitation induces the redox reaction while the ligand field transition excitation induces the catalysed dehydration and decomposition.

Introduction

While the photochemical properties of ferrocene (Fc) and its derivatives are well known [1] and widely used [2], very few studies are concerned with the photochemical properties of its oxidized form ($Fc^{\bullet+}$). Three behaviours have been observed for the ferrocenium derivative: the photoreduction of ferrocenium ($Fc^{\bullet+}$) to Fc [3, 4], its photodecomposition [3, 4] and an oscillatory process [5, 6]. Generally photochemical products other than ferrocene have not been identified.

On the other hand, improvements in the knowledge of the photochemical properties of organic radical cations [7] prompte us to study the photochemical behaviour of an organometallic radical cation like $Fc^{\bullet+}$ and its decamethylated derivative $DMFc^{\bullet+}$ in order to observe a possible influence of the metal. Thus the electronic transitions produced by visible photo absorption are of different natures, either localized on the metal (dd), or ligand to metal charge transfer (LMCT) [8].

This study shows that $Fc^{\bullet+}$ is able to have an analogous behaviour to the organic radical cations under visible light irradiation in the presence of phenylated alcohols. Its oxidizing properties are enhanced and the oxidation of benzylalcohol into benzaldehyde has been observed. Moreover $Fc^{\bullet+}$ can act as a Lewis acid: in the presence of benzhydrol, the symmetrical ether has been isolated and this reaction is catalytic in $Fc^{\bullet+}$.

Experimental

Acetonitrile is purified as described previously [7] and redistilled on P_2O_5 before being stored under argon. Solution preparations were performed under argon in a glove bag. In earlier work deoxygenation of the different solvents and substrates was effectuated by successive argon purges using a two opening gas-tight chamber.

The ferrocenium hexafluorophosphate ($FcPF_6$) was synthesized from sublimed ferrocene as described previously [9]. The same procedure was used for the decamethylferrocenium hexafluorophosphate ($DMFcPF_6$). The benzylalcohol, benzhydrol, propanol-1, benzaldehyde were purchased and purified and the benzhydryl oxide was prepared and purified as described previously [7].

The photochemical, spectrophotochemical and spectrometric devices and methods as well as HPLC technique have been detailed in a previous paper [10]. The short-wavelength cut-off filter ($\lambda > 400$ nm) is an aqueous solution of $NaNO_2$ 180 g l^{-1}.

Photolysis of $FcPF_6$ and $DMFcPF_6$ in Presence of Benzylalcohol or Benzhydrol

All the photolyses were carried out according to the following characteristic procedures.

(a) $FcPF_6$ (43.6 mg; 2.6×10^{-3} M) and benzylalcohol (1 cm^3; 1.9×10^{-1} M) are dissolved in 50 cm^3 of acetonitrile: half the solution is irradiated for 1 h ($\lambda > 300$ nm) while the blank solution is stored in the dark. The irradiated and the blank solutions are similarly treated: the solvent is evaporated under reduced pressure and the organic substrates are extracted with diethyl oxide. Then the obtained solution is filtered and evaporated to dryness, and the residue is dissolved in the elution solvent (dichloromethane/n-heptane 17/83). The HPLC dosage carried out on a silica column indicated that 2.2 mg (8.3×10^{-4} M) of benzaldehyde are produced in

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the irradiated solution and 0.8 mg (3.01×10^{-4} M) in the blank solution.

(b) $FcPF_6$ (42 mg) and benzhydrol (1.27 g) are dissolved in 50 cm^3 of acetonitrile; half the solution is irradiated for 6 h 30 min ($\lambda > 400$ mm) while the blank solution is stored in the dark. The irradiated and the blank solution are treated and dried as described above. The HPLC dosage indicates the formation of 359 mg of benzhydryl oxide in the irradiated solution and only 54 mg in the blank solution.

Photolysis of $FcPF_6$ in Presence of Propanol-1

$FcPF_6$ (40.5 mg) and propanol-1 (20 cm^3) are dissolved in 25 cm^3 of acetonitrile, 25 cm^3 of the solution are irradiated for 2 h 30 min ($\lambda > 300$ nm). The comparison of the visible absorption spectra of the initial, blank and irradiated solution shows that all the ferricinium is reduced to ferrocene. Several attempts for characterizing and dosage of propanal by VPC of HPLC were unsuccessful.

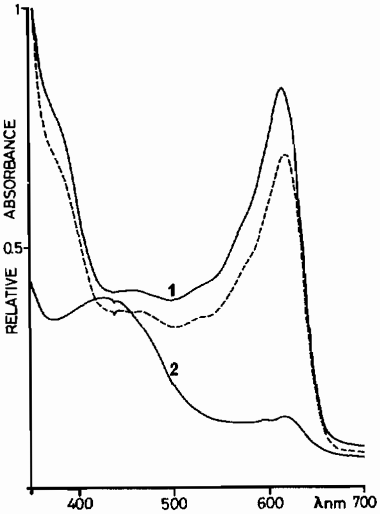

Fig. 1. UV–Vis absorption spectra of an $Fc^{\cdot+}$ solution in acetonitrile propanol-1 (1.25:1) mixture: curve 1, before photolysis; curve 2, after photolysis; -----, blank solution.

Results

The irradiations of $Fc^{\cdot+}$ were carried out in acetonitrile in the presence of benzylalcohol, benzhydrol or propanol-1. It has been reported in the literature that $Fc^{\cdot+}$ solutions are unstable in the presence of nucleophilic species [6, 11] or trace amounts of solvated oxygen [12]. However it has also been reported that a stable solution of $Fc^{\cdot+}$ in acetonitrile can be obtained in an oxygen free atmosphere [11, 12]. Therefore, all the solutions were prepared under an inert atmosphere (see 'Experimental') using hexafluorophosphate ion as the counterion.

In spite of these precautions during the experimental procedure, some instability has been observed. Consequently, all the results of the irradiation have been compared to those of a blank solution stored in the dark. Each data gathers the results of several photolyses and several dosages in order to ensure its reproducibility. The photoreduction and photodecomposition of $Fc^{\cdot+}$ were observed by UV–Vis absorption spectrophotometry. The concentration of $Fc^{\cdot+}$ is evaluated at 615 nm where only $Fc^{\cdot+}$ absorbs and the formation of Fc by analysing the absorbance at 435 nm using 95 and 110 cm^{-1} mol^{-1} l as molecular extinction coefficients for Fc and $Fc^{\cdot+}$ respectively. The chemical composition of the organic substrates is analysed by HPLC.

Photolysis of $Fc^{\cdot+}$ in Propanol-1

The UV–Vis absorption spectra of a ferrocenium solution 2.72×10^{-3} M in acetonitrile/propanol-1 (1.25:1) recorded during the photolysis at $\lambda > 300$ nm are reported in Fig. 1. The solution obtained after irradiation for 2 h 30 min is green because there is some $Fc^{\cdot+}$ left. All $Fc^{\cdot+}$ that can no longer be seen has been converted into Fc. Different attempts to characterize propanal-1 failed.

Irradiation of Ferrocenium and Decamethylferrocenium in Presence of Benzylalcohol

1 hour irradiation at a higher wavelength than 300 nm of a solution of ferrocenium 2.4×10^{-3} M and benzylalcohol 1.9×10^{-1} M in acetonitrile produces the photoreduction of ferrocenium to ferrocene with 85% yield (Fig. 2). After treatment of the medium, HPLC titration indicates the presence of benzaldehyde with 40% yield relative to the initial ferrocenium amount according to the following reaction

$$2Fc^{\cdot+} + C_6H_5CH_2OH \longrightarrow C_6H_5CHO + 2Fc + 2H^+$$

An irradiation at $\lambda > 330$ nm for 21 h also induces the ferrocenium disparition but the ferrocene is produced with only 75% yield. The HPLC titration indicates the presence of benzaldehyde.

If the irradiation is carried out at $\lambda > 366$ nm for 71 h, slight ferrocenium decomposition (25%) is observed. Ferrocene is not formed because the irradiated solution shows the blue color characteristic of the ferrocenium ion (Fig. 2) and no alcohol oxidation is observed.

Photolysis of a solution of $DMFc^{\cdot+}$ in the same concentration conditions at $\lambda > 300$ nm for 10 days causes no change in the solution.

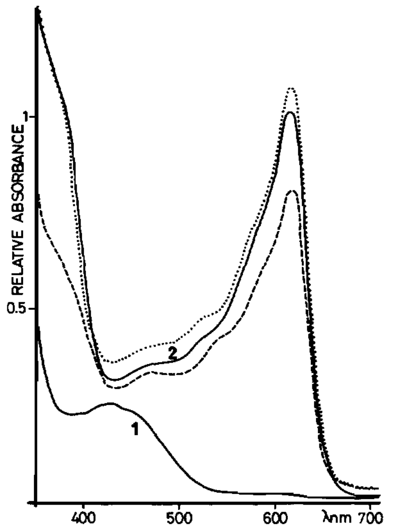

Fig. 2. UV–Vis absorption spectra of an $Fc^{\cdot+}$ and benzylalcohol solution in acetonitrile: ·····, before photolysis; curve 1, after 1 h of photolysis with λ > 300 nm; -----, after 71 h of photolysis with λ > 366 nm; curve 2, blank solution after 71 h.

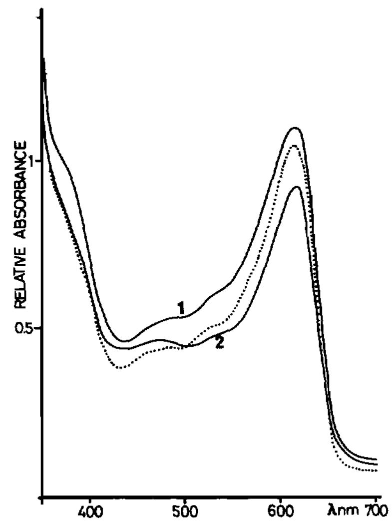

Fig. 3. UV–Vis absorption spectra of an $Fc^{\cdot+}$ and benzhydrol solution in acetonitrile: curve 1, before photolysis; curve 2, after 6 h 30 min of photolysis at λ > 400 nm; ·····, blank solution.

In all these photolysis experiments, no ether oxide formation was detected within the limits of our experimental procedure.

Photolysis of Ferrocenium and Decamethylferrocenium in Presence of Benzhydrol

The photolysis of $Fc^{\cdot+}$ was carried out at wavelengths higher than 400 nm because the absorption of benzhydrol is negligible and the absorption of light energy does not produce the photoreduction of $Fc^{\cdot+}$ in this wavelength range.

The UV–Vis absorption spectra of the irradiated and the blank solutions of ferrocenium 2.5×10^{-3} M and benzhydrol 1.4×10^{-1} M, in acetonitrile, show that $Fc^{\cdot+}$ remains almost unchanged (Fig. 3) throughout the irradiation. The HPLC analysis indicates the formation of benzhydryl oxide at a 4×10^{-2} M concentration, *i.e.* 57% yield relative to the initial alcohol.

When a solution of decamethylferrocenium 2.4×10^{-3} M and benzhydrol 1.3×10^{-1} M is photolysed for 7 days, the $DMFc^{\cdot+}$ remains stable and the yield of the other oxide (<1%) is very low. In all these photolysis experiments, no ketone formation was detected within the limits of our experimental procedure.

Discussion

When one compares the photoinduced reactions of ferrocenium with those of the organic radical cation in alcoholic media, the following observations can be made. Like other organic radical cations of low redox potential, ferrocenium needs visible light energy to oxidize the benzylalcohol to benzaldehyde and acts as a Lewis acid towards benzhydrol. Conversely, ferrocenium is reduced in the presence of propanol-1 under the action of UV–Vis light.

Looking at the results of the irradiation of ferrocenium in the presence of benzylalcohol and propanol-1 the yield of benzaldehyde is very low and propanal is not detected. However, in dealing with organic radical cations, their electrochemical synthesis and their low sensitivity to oxygen, allowed the authors to regenerate them several times during the photolysis, so that the benzaldehyde amounts were accumulated and immediately titrated in the reaction medium. In the case of ferrocenium, the loss of some of the benzaldehyde and the absence of detection of propanal (see 'Experimental') is not surprising. However the amount of benzaldehyde is well detected within the limits of our experimental procedure, and is higher in the irradiated solution in the presence of ferrocenium than in its absence [7]. The results of the irradiations in different wavelength ranges in the case of benzylalcohol allowed us to specify the nature of the electronic transition which initiates the photoreduction and the photodecomposition of $Fc^{\cdot+}$. The photoreduction occurs when irradiating at wavelengths lower than 400 nm. In this field, the light energy absorption produces a ligand to metal charge transfer transition being able to initiate the intermolecular electron transfer reaction leading to Fc. This observation could explain the photoreduction of ferrocenium in propanol-1 while no reaction of organic radical cations is observed with aliphatic primary alcohols. The photodecomposition is produced by the irradiation at wavelengths higher than 400 nm, which corresponds to the ligand field transitions [8] of ferrocenium. It is generally assumed that the consequence of the absorption in the ligand field is a weakening of the metal–ligand bond, which promotes substitutions reactions or, as in this case, decomposition.

No photoreactions of $DMFc^{\cdot+}$ in the presence of benzylalcohol were observed, probably because of sterical crowding.

Towards benzhydrol and under irradiation, ferrocenium shows an analogous behaviour to organic radical cations [7]. No ketone is detected although benzhydrol is more easily oxidizable than benzylalcohol. Only the ether oxide with 57% yield relative to the initial alcohol is produced and this reaction is catalytic in $Fc^{\cdot+}$.

$$2(C_6H_5)_2CHOH \xrightarrow[\lambda > 400\,nm]{Fc^{\cdot+}} C_6H_5\text{-}CH\text{-}O\text{-}CH\text{-}C_6H_5$$

As the ferrocenium was synthesized in acidic medium, participation of residual protons to the formation of ether oxide was not likely to occur [7], although could not be completely eliminated. On the other hand, the ether oxide formation is very sensitive to the steric hindrance [7]. Therefore, an irradiation of decamethylferrocenium, synthesized in a similar procedure to ferrocenium, was carried out in the presence of benhydrol. The detected yield of ether oxide was very low (<1%), which corroborates the view that the Lewis acid properties of ferrocenium are enhanced under irradiation.

Conclusions

The irradiation of $Fc^{\cdot+}$ in the LMCT absorption bands of high energy produces the oxidation of benzylalcohol, and contrariwise to other organic radical cations, of propanol-1. On the other hand, the irradiation in the ligand field absorption bands induces properties of a Lewis acid and/or decomposition of $Fc^{\cdot+}$. The benzylalcohol is too weak a Lewis base to produce the ether, while the ether is formed by catalysis in the benzhydrol, a fact which was observed in the case of the organic radical cations.

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