

Reactivity of ferrocenium cations with molecular oxygen in polar organic solvents: Decomposition, redox reactions and stabilization

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Abstract

The behaviour of chemically or electrochemically generated ferrocenium cations has been studied in some polar organic solvents (DMF, DMSO, acetonitrile, acetone, methylene chloride) under molecular oxygen. Adducts between oxygen and ferrocenium species can differently evolve according to the solvent (oxidizable or not) and the absence or the presence of another reagent. A rapid decomposition of ferrocenium cations is observed in the absence of another substrate. In the presence of some substrates and antioxidants, the stability of ferrocenium cations towards molecular oxygen notably increases and in some cases redox reactions take place with formation of ferrocene.

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1. Introduction

The decomposition of ferrocenium cations in organic solvents was reported a long time ago [1]. The nucleophilic character of the solvent was previously proposed to explain the reactivity of ferrocenium species in organic solvents [2,3]. It was observed that ferrocenium cations decomposed more rapidly in DMSO or DMF than in acetone or acetonitrile. Later, by using electrochemistry, Sato et al. [4] underscored the role of molecular oxygen about this instability. The cyclic voltammogram of an oxygen free solution of ferrocene in DMSO showed the typical ferrocene/ferrocenium reversible system, while in the presence of oxygen, a loss of reversibility was observed. Quasi similar cyclic voltammograms were

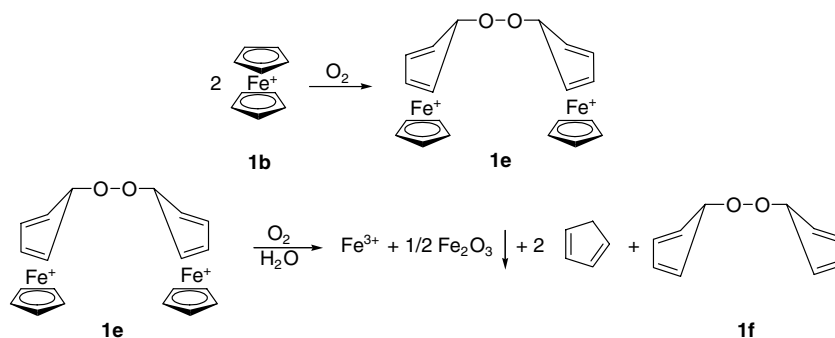
observed in DMF but not in acetonitrile, acetone or methylene chloride [5]. However, at a higher time scale than cyclic voltammetry, the decomposition of chemically or electrochemically generated ferrocenium cations was observed in these latter solvents. The influence of molecular oxygen and the specific role of the solvent were highlighted during the anodic oxidation of $\text{Cr}(\text{CO})_5\text{CN}^-$ anions [6]. More recently, Zotti et al. [7] studied the oxygen-decomposition of ferrocenium cations in acetonitrile and suggested a decomposition mechanism which involved an unstable dimeric complex **1e** with an oxygen bridge between two cyclopentadiene rings (Scheme 1).

The presence of this initially produced complex could explain the trapping of cyclopentadienols by strong dienophiles during the decomposition of various ferrocenium cations in acetonitrile [8].

This paper is devoted to a general study of the behaviour of ferrocenium species in polar organic solvents in

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the presence of oxygen and various reagents (oxidizable species and anti-oxygen). Particularly, new intermediates are proposed to explain the reactivity or the stabilization of ferrocenium cations in the presence of some reagents and molecular oxygen.

2. Results

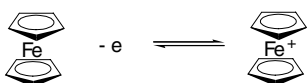
2.1. Cyclic voltammetry of ferrocenes in the presence of oxygen

2.1.1. In DMF or DMSO

As previously reported [4,5], the cyclic voltammogram at a platinum or a glassy carbon electrode of ferrocene **1a** in an oxygen-saturated solution of DMSO or DMF does not show the reversible system (Scheme 2) normally observed under nitrogen at a scan rate of 0.1 V s^{-1} .

In the presence of oxygen, the anodic wave increases while the cathodic wave decreases and a new irreversible cathodic wave appears at a lower potential ($E_{p_c} \# -0.45 \text{ V}_{\text{SCE}}$). The phenomenon is less pronounced with 1,1'-dimethylferrocene **2a** in an oxygen-saturated solution of DMF, the cathodic wave continuously decreases with the appearance of an irreversible cathodic wave at $E_{p_c} \# -0.40 \text{ V}_{\text{SCE}}$ after a repetitive cycling. Conversely, a complete reversibility is again observed for decamethylferrocene in an oxygen-saturated solution of DMF. The great stability of octamethyl- and decamethylferrocenium cations in acetonitrile under oxygen was previously observed [9].

After addition of a stoichiometric amount of triphenylphosphine or 1,3-diphenylisobenzofuran to the oxygen saturated DMF solution, ferrocene **1a** is reversibly oxidized ($E_{p_a} = 0.53 \text{ V}_{\text{SCE}}$, $E_{p_c} = 0.44 \text{ V}_{\text{SCE}}$,



Scheme 2.

$I_{p_c}/I_{p_a} = 1$). However, when the scan is anodic enough to oxidize triphenylphosphine ($E_{p_a} = 1.08 \text{ V}_{\text{SCE}}$) or diphenylisobenzofuran ($E_{p_a} = 0.75 \text{ V}_{\text{SCE}}$), a loss of the reversible ferrocene/ferrocenium system **1a/1b** is observed. Moreover compounds often used as antioxidants in industry (phenols or amines) proved to be efficient for stabilizing ferrocenium cations **1b** in DMF under oxygen. In this way, by adding 2,6-diterbutyl-4-methylphenol (ionol) in ionol/ferrocene molar ratio ≥ 1 or *N*-cyclohexyl-*N'*-phenyl-1,4-benzene diamine (flexzone 6H) in flexzone/ferrocene molar ratio ≥ 0.5 , a complete reversibility of the system ferrocene/ferrocenium **1a/1b** and a total disappearance of the cathodic wave located at $-0.45 \text{ V}_{\text{SCE}}$ are observed in DMF saturated in oxygen. It is worth noting that flexzone and ionol are irreversibly oxidized before ferrocene ($E_{p_a} = 0.34 \text{ V}_{\text{SCE}}$) and after ferrocene ($1.65 \text{ V}_{\text{SCE}}$), respectively.

2.1.2. In acetonitrile, acetone or methylene chloride

In oxygen-saturated solutions of acetonitrile, acetone or methylene chloride, the electrogenerated ferrocenium cations **1b** appear practically stable at the time scale of cyclic voltammetry (0.1 V s^{-1}). However, as reported by Daschbach [10] and later by Zotti et al. [7], the current intensities of the anodic and cathodic peaks continuously decrease during a repetitive scanning, with at the same time, formation of a yellowish deposit on the electrode.

2.2. Reactivity of ferrocenium cations in the presence of oxygen

2.2.1. In DMF or DMSO

2.2.1.1. In the absence of reagents. In DMF or DMSO, the blue color of ferrocenium cations **1b** instantaneously turns orange on addition of oxygen. At the same time, the disappearance of the initial cathodic wave ($(E_{1/2})_c = 0.48 \text{ V}_{\text{SCE}}$, in DMF) of ferrocenium cations and the appearance of an anodic wave ($(E_{1/2})_a = 0.50 \text{ V}_{\text{SCE}}$) attributable to the ferrocene oxidation, are observed at a platinum rotating disc electrode. The height of the latter wave is half of the former. After work up, ferrocene

1a was isolated in 47% yield from the DMF solution and characterized. Previously, Prins et al. [2] observed a rapid decomposition of ferrocenium cations in DMF, DMSO and HMPTA with formation of ferrocene in 50% yield determined by spectrophotometric measurements. The role of oxygen in the decomposition was not considered.

2.2.1.2. In the presence of oxidizable reagents. As predictable by cyclic voltammetry, the stability of ferrocenium cations in DMF, under oxygen, increases by adding stoichiometric amounts of triphenylphosphine or 1,3-diphenylisobenzofuran to the solution. Ferrocene **1a** is quantitatively produced as shown by voltammetry at a rotating disc electrode, whereas triphenylphosphine or diphenylisobenzofuran are oxidized (Figs. 1 and 2). It is worth noting that under inert atmosphere of nitrogen, the redox reaction is very slow (Fig. 2) and could result from trace amounts of dissolved oxygen. The oxidation of triphenylphosphine did not give triphenylphosphine oxide (absence of absorption frequency at 1190 cm^{-1}) but probably a phosphonium salt as proposed for electrochemical oxidation of triphenylphosphine in non aqueous media [11]. One mole of 2-benzoylbenzophenon was obtained per mol of ferrocenium cations after indirect oxidation of diphenylisobenzofuran (Scheme 3). A quantitative formation of ferrocene shows that the proposed intermediate **1e** [7] cannot be retained as oxidizing species.

2.2.2. In acetonitrile, acetone or methylene chloride

2.2.2.1. In the absence of reagents. In oxygen saturated solution of acetonitrile, acetone or methylene chloride, ferrocenium cations **1b** totally disappear in few minutes with formation of a brown precipitate and a light brown solution as previously observed [5,7]. Ferrocene **1a** was

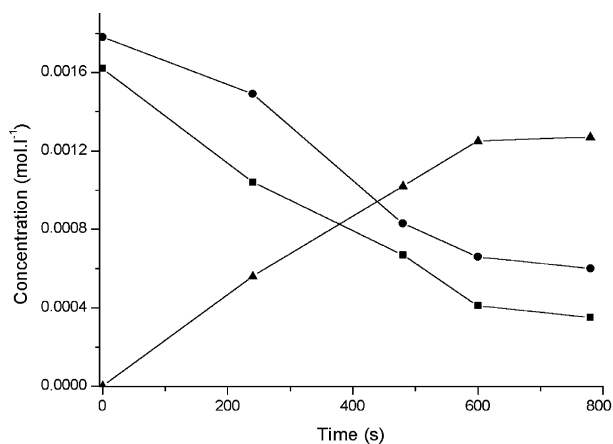


Fig. 1. Redox reaction between ferrocenium cations **1b** and triphenylphosphine in DMF + 0.1 M Bu_4NBF_4 under oxygen. ●, triphenylphosphine disappearance; ■, ferrocenium disappearance; ▲, ferrocene formation.

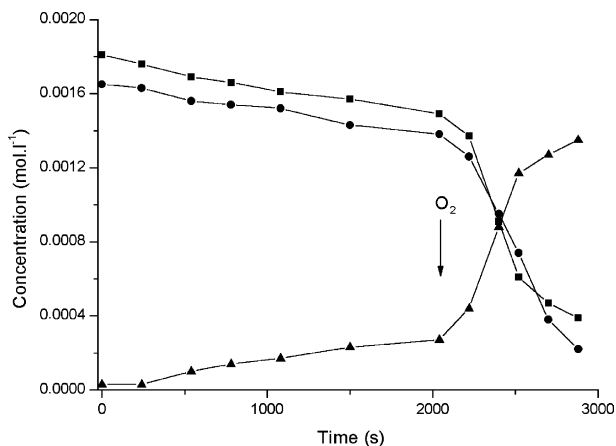


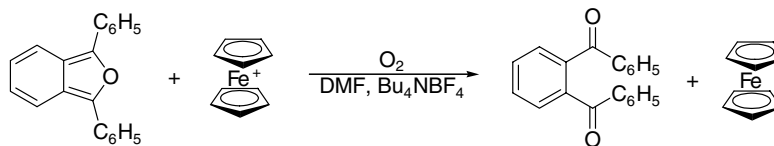
Fig. 2. Redox reaction between ferrocenium cations **1b** and 1,3-diphenylisobenzofuran in DMF + 0.1 M Bu_4NBF_4 . Under nitrogen until 2070 s, then oxygen. ●, diphenylisobenzofuran disappearance; ■, ferrocenium disappearance; ▲, ferrocene formation.

not detected after decomposition. Moreover, we observed that ferrocene **1a** and ferrocenium cations **1b** simultaneously disappear from a mixture of these two compounds in acetonitrile under oxygen (Fig. 3). The rates of disappearance were dependent on the ratio ferrocene/ferrocenium.

2.2.2.2. In the presence of oxidizable reagents. The rate of ferrocenium cation **1b** disappearance is notably slowed down by adding triphenylphosphine to an oxygen saturated solution of acetonitrile containing the former compound (Figs. 4 and 5). This rate decreases with increasing the ratio triphenylphosphine/ferrocenium cations. As an example, for triphenylphosphine/ferrocenium ratios equal to 1.06 and 1.6, about 25% of ferrocenium cations are reduced into ferrocene after 25 mn and 3 h, respectively. With a triphenylphosphine/ferrocenium cations ratio less than 1, a rapid decomposition was observed after a quasi complete transformation of triphenylphosphine (Fig. 5).

A mixture of ferrocenium cations **1b** and 1,3-diphenylisobenzofuran (molar ratio 1/1) in acetonitrile appears totally stable after one hour under oxygen. The cathodic wave of ferrocenium cations and the anodic wave of diphenylisobenzofuran are not altered.

As previously shown by cyclic voltammetry (cf. Section 2.1.1), the addition of antioxidants (ionol, flexzone 6H) to solutions of ferrocene **1a** under oxygen, avoids the rapid decomposition of electrogenerated ferrocenium cations **1b**. Flexzone shows a higher efficiency than ionol to stabilize ferrocenium cations **1b** in acetonitrile under oxygen. In this way, we do not observe any decomposition of ferrocenium cations in the presence of small amounts of flexzone (molar ratio flexzone/ferrocenium 3.5%) after 3 h at room temperature, then heating at $60\text{ }^\circ\text{C}$ for 4 h (neither change in the blue color nor



Scheme 3.

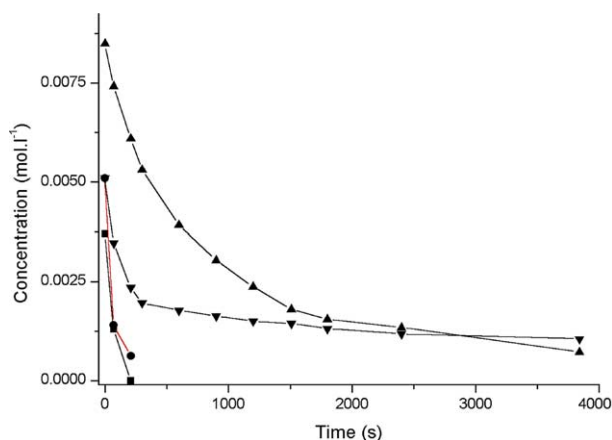


Fig. 3. Chemical decomposition of a mixture ferrocene **1a** + ferrocenium cations **1b** in acetonitrile + 0.1 M Bu_4NBF_4 under oxygen. Ferrocene/ferrocenium molar ratio 0.72: ●, ferrocenium disappearance; ■, ferrocene disappearance. Ferrocene/ferrocenium molar ratio 1.67: ▼, ferrocenium disappearance; ▲, ferrocene disappearance.

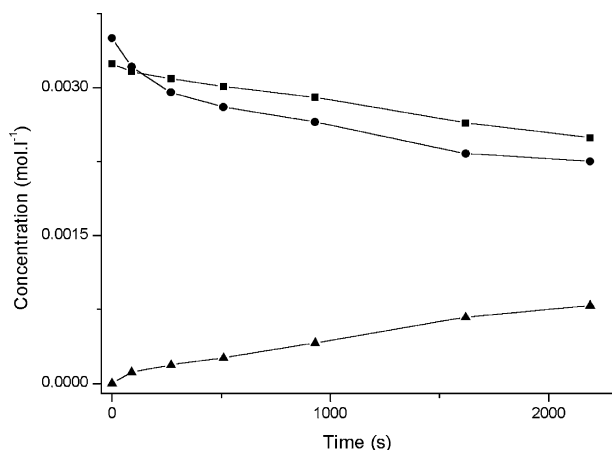


Fig. 4. Redox reaction between ferrocenium cations **1b** and triphenylphosphine in acetonitrile + 0.1 M Bu_4NBF_4 , under oxygen. ●, triphenylphosphine disappearance; ■, ferrocenium cations disappearance; ▲, ferrocene formation.

modification of the cathodic wave). We only observe the decomposition of ferrocenium cations after heating at 60 °C for 4.5 h. With the same amount of ionol, ferrocenium cations are decomposed in few minutes at room temperature.

In oxygen-saturated solution of acetonitrile containing lithium hydroxide to generate phenate anions, a redox reaction between ferrocenium cations **1b** ($E_{1/2} =$

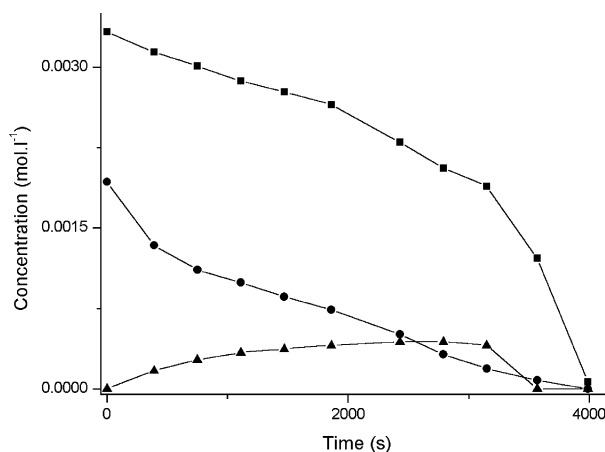


Fig. 5. Decomposition of ferrocenium cations **1b** in the presence of triphenylphosphine in acetonitrile + 0.1 M Bu_4NBF_4 , under oxygen. ●, triphenylphosphine disappearance; ■, ferrocenium cations disappearance; ▲, ferrocene formation.

0.51 V_{SCE}) and ionol ($E_{1/2} = 1.3 V_{\text{SCE}}$) quantitatively gives ferrocene **1a** (Fig. 6). In order to avoid a possible decomposition of ferrocenium cations, flexzone was added (molar ratio flexzone/ferrocenium 3.5%). We controlled the lack of the redox reaction between **1b** and ionol under nitrogen in the same medium. A similar redox reaction takes place between ferrocenium cations **1b** and

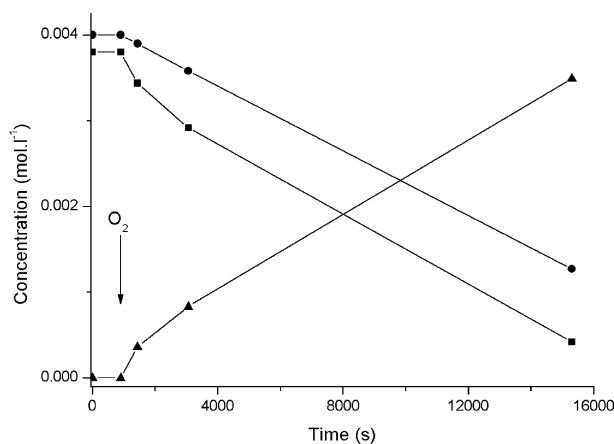
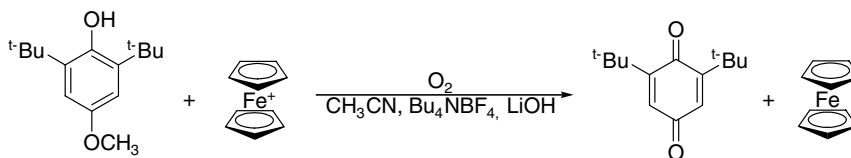


Fig. 6. Redox reaction between ferrocenium cations **1b** and 2,6-diterbutyl-4-methyl phenol (ionol) in the presence of flexzone (1.4×10^{-4} M); acetonitrile + 0.1 M Bu_4NBF_4 , LiOH saturated. Under nitrogen until 900 s, then oxygen. ●, ionol disappearance; ■, ferrocenium disappearance; ▲, ferrocene formation.



Scheme 4.

3,5-diterbutyl-4-hydroxy anisole ($E_{1/2} = 0.98 \text{ V}_{\text{SCE}}$) in the same oxygen-saturated medium (Scheme 4).

The oxidation rate for the latter compound (about 40% oxidized after 1 h) is higher than for ionol (about 15% oxidized after 1 h). After complete reactions, 70% and 85% of ionol and 3,5-diterbutyl-4-hydroxyanisole respectively were oxidized when ferrocenium cations were totally reduced. 2,6-diterbutyl-1,4-benzoquinone was obtained and characterized from the latter phenol.

2.2.2.3. In the presence of a dienophile. In order to trap cyclopentadiene derivatives resulting from the decomposition of ferrocenium cations, we used 4-phenyl-1,2,4-triazoline-3,5-dione **3b** known as a powerful dienophile [12,13]. Ferrocenium cations **1b** and the dienophile **3b** were prepared from a co-oxidation in a flow cell fitted with a porous anode, of ferrocene **1a** and 4-phenyl-1,2,4-triazolidine-3,5-dione (4-phenylurazole) **3a** in acidified acetonitrile [8]. A decomposition of ferrocenium cations **1b** occurred after adding solid sodium carbonate to the electrolyzed solution under oxygen (Scheme 5). The decomposition is complete after 1 h. When aqueous solutions of sodium carbonate are used, ferrocene is produced by a redox reaction. It is worth noting that in acidic acetonitrile, ferrocenium cations **1b** are stable under oxygen; however after adding solid sodium carbonate in order to neutralize the acidic medium, decomposition is obtained in few minutes in the absence of dienophile **3b**.

Two adducts **1c** and **1d** resulting from reactions between the dienophile and cyclopentadien-5-yl and cyclopentadiene respectively were isolated and characterized. The quantity of adduct **1c** notably increases as the dienophile–ferrocenium cations ratio increases, when the quantity of adduct **1d** is nearly constant (Table 1).

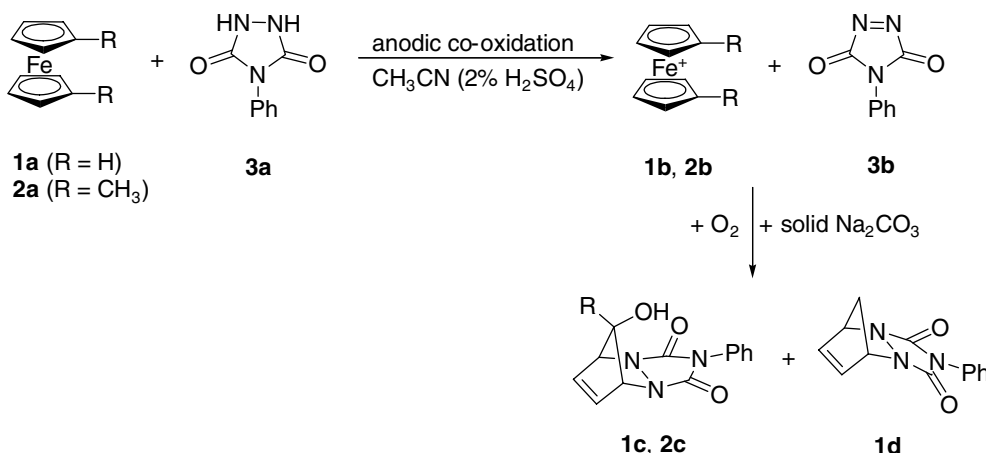
Addition of methanol (2.5% in volume) to the mixture of ferrocenium **1b** and dienophile **3b** in acetonitrile before decomposition, gives again **1c** and **1d** after decomposition without formation of a methoxylated adduct.

In the same way [8], 1,1'-dimethylferrocenium cations **2b** give **2c** in 41% yield. **2b** decompose more slowly than ferrocenium cations **1b**.

2.3. Controlled potential electrolyses of ferrocene **1a** in the presence of oxygen

2.3.1. In DMF or DMSO

Macroscale electrolyses at a platinum or a glassy carbon anode (working potential 1 V_{SCE}) of ferrocene **1a** in an oxygen-saturated solution of DMF, involve 2 F per mol. A rapid decomposition of the produced ferrocenium **1b** occurs with simultaneously formation of CO_2 which can be trapped by bubbling in a solution of calcium hydroxide or sodium hydroxide for dosage in the latter case. About 0.45 mol of CO_2 is produced per mol of starting ferrocene. It is worth noting that, for the chemical decomposition of ferrocenium cations in



Scheme 5.

Table 1

Adducts **1c** (with cyclopentadienol) and **1d** (with cyclopentadiene) resulting from the decomposition of ferrocenium cations **1b** in the presence of 4-phenyl-1,2,4-triazoline-3,5-dione **3b** in acetonitrile under oxygen

3b/1b molar ratio	Adducts (% yield ^a)	
1:1	1c (46)	1d (12)
2:1	1c (69)	1d (14)
3:1	1c (80)	1d (15)

^a Calculated from initial ferrocene **1a**.

DMF under oxygen, without electrolysis (cf. 2.2.1), no CO₂ evolution occurred. Attempt to characterize dimethylamine failed. During the electrolysis the initial orange color of the solution turns red.

Electrolyses of ferrocene **1a** performed in oxygen-saturated solution of DMSO consume approximately 2.5 F per mol of starting substrate. A rapid decomposition of the electrogenerated ferrocenium leading to a red solution is observed without production of CO₂.

No products were isolated from solutions after electrolyses in DMF and DMSO.

2.3.2. In acetonitrile, acetone or methylene chloride

2.3.2.1. In the absence of reagents. Anodic oxidations of ferrocene **1a** in an oxygen-saturated solution of acetonitrile, acetone or methylene chloride involve 0.3–0.5 F per mol according to the amount of starting substrate. A clear to dark brown solid precipitates during the electrolyses. Elemental analyses of these solids isolated after electrolyses in acetonitrile or methylene chloride containing Bu₄NBF₄ as electrolyte (Table 2) revealed a difference of Fe/F ratio between the two solvents. Fe content is higher and F content is lower in acetonitrile than in methylene chloride. Solids are slightly soluble in water and soluble in nitric or hydrochloric acid. Characteristic colors of ferric complexes with thiocyanate ions or hexacyanoferrate (II) are only observed after acidification. After adding sodium hydroxide to the acidic solution and filtration of ferric hydroxide, the resulting solution presents acido-basic properties characterized by a reversible change of colours (orange-yellow in acidic medium and deep red in basic medium). Solids decompose for temperature higher than 250 °C, giving a black powder. When electrolyses are performed in the presence of Bu₄NClO₄ as electrolyte, the isolated precipitate explodes for temperature higher than 250 °C.

Table 2

Elemental analyses of isolated solids after electrolyses of ferrocene **1a** in acetonitrile (a) or methylene chloride (b) + 0.1 M Bu₄NBF₄, under oxygen

Solvent	C%	H%	N%	Cl%	Fe%	F%
(a)	22.95	3.54	0.10	–	31.62	4.63
(b)	23.70	3.70	–	1.67	23.55	7.40

2.3.2.2. In the presence of oxidizable reagents. The electrolysis at 0.7 V_{SCE}, under oxygen, of ferrocene **1a** (2 mmol) in acetonitrile + LiClO₄ containing triphenylphosphine (2 mmol) leads to a blue solution after consumption of 1 F per mol of ferrocene with a significant decreasing of the current intensity (more than 90% relatively to the initial current). The characteristic blue color of ferrocenium cations **1b** was persistent until consumption with residual current of 3–3.5 F per mol of ferrocene, then a change of color occurs. At this time, the anodic wave of triphenylphosphine and the cathodic wave of ferrocenium cations totally disappear.

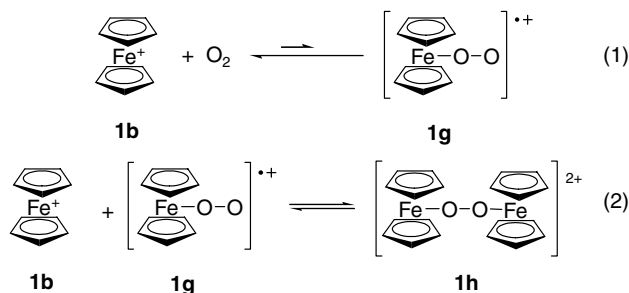
A similar electrolysis of ferrocene **1a** (2 mmol), performed at 0.6 V_{SCE}, in the presence of 1,3-diphenylisobenzofuran (2 mmol) instead of triphenylphosphine, involved 1 F per mol of ferrocene with a residual current corresponding to 5% of the initial current. Then the anodic wave of diphenylisobenzofuran very slowly decreased (less than 15% after one night) without decomposition of electrogenerated ferrocenium cations **1b** characterized by their cathodic wave.

3. Discussion

3.1. Oxidation of organic substrates by ferrocenium-oxygen adducts

In order to account the experimental results, the initial oxygen attack on ferrocenium cations cannot involve a direct coupling with the cyclopentadienyl ring leading to **1e** (Scheme 1) as previously proposed [7,9] by analogy with products resulting from reactions between oxygen and 19-electron complexes of cobalt [14] or iron [15,16]. In this last case, the proposed coupling reaction between molecular oxygen and 19-electron complexes takes place through a redox reaction followed by a nucleophilic attack of O₂^{•-} at arene ligands of oxidized 18-electron complexes [16]. In fact, ferrocene quantitatively produced by a redox reaction between oxidizable substrates and ferrocenium cations under oxygen cannot result from the reduction of **1e**. In that case, the radical coupling reaction probably takes place at the iron center affording a μ-peroxy iron radical cation **1g** (Eq. 1) and (or) a μ-peroxo di-iron complex **1h** (Eq. 2) (Scheme 6). μ-peroxo di-iron complexes have been frequently proposed as unstable intermediates. A first detection and characterization of a such intermediate was made in the autoxidation of ferrous porphyrins [17]. In a preliminary communication [5], we suggested **1h** as intermediate in the decomposition of ferrocenium cations in polar organic solvents under oxygen.

The first radical coupling (Eq. 1) is probably an equilibrium in which the concentration of complex **1g** is very low. To argue this assertion, the stabilization of ferrocenium cations, particularly in acetonitrile, is obtained



Scheme 6.

after adding small amounts of an active antioxidant (flexzone).

In order to explain the role of flexzone, an hypothetical formation of singlet oxygen which is a powerful oxidizing reagent, can be considered. It is well known that flexzone inhibits singlet oxygen; as an example, flexzone totally suppressed singlet oxygen produced in the photo-oxidation of non vulcanized rubbers [18]. However, our experimental results are not in accordance with the presence of singlet oxygen. Diphenylisobenzofuran which has a larger rate constant for quenching singlet oxygen [19] affording benzoylbenzophenon, does not react (or very slowly) in acetonitrile containing ferrocenium cations under oxygen. Nevertheless, it was previously found [20] that singlet oxygen generated in acetonitrile from a redox reaction between ferrocenium cation and superoxide anion both prepared by pulse electrolysis, was trapped by diphenylisobenzofuran. Moreover, an oxidation of substrate by hypothetical singlet oxygen resulting from the equilibrium (1) would not give ferrocene.

In the presence of some oxidizable substrates, complexes **1g** or **1h** act as oxidizing reagents. We observed that under oxygen, one mole of ferrocenium cations which is reduced into ferrocene, practically oxidizes one mole of diphenylisobenzofuran in DMF (Fig. 2) or one mole of phenols in acetonitrile (Fig. 6). It is worth noting that a catalytic oxidation of residual water in the medium, can explain the incomplete oxidation of phenols (#90%). We controlled that ferrocenium cations were reduced into ferrocene in aqueous basic media under oxygen; the rate of this reaction increases with the pH values. Oxidations of phenols generally involve 2F per mol, consequently reductions of **1g** or **1h** would consume 2F or 4F, respectively. Phenols were used as chain-

breaking antioxidants for many years and the supposed mechanism involves a reaction with peroxy radicals [21]. By analogy, we can propose **1g** instead of **1h** as oxidizing reagent as exemplified in Scheme 7 for phenate ions.

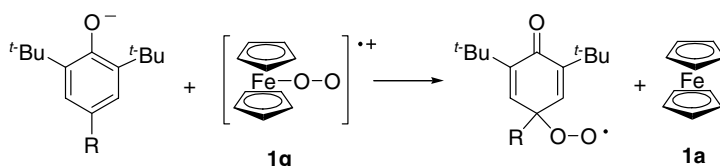
The new peroxy radical issued from phenate ion decomposes affording the final product. Oxidations of triphenylphosphine or diphenylisobenzofuran can take place according to a similar mechanism involving **1g**. The oxidation rate is higher in DMF than in acetonitrile (cf. Figs. 1 and 4 for triphenylphosphine). This observation can explain the apparent stability of diphenylisobenzofuran and ferrocenium cations in acetonitrile under oxygen for one hour (cf. 2.2.2.2) and a very slow disappearance of diphenylisobenzofuran during the electrolysis of ferrocene in acetonitrile in the presence of oxygen (cf. 2.3.2.2).

In the presence of an antioxygen (flexzone), the oxidizing properties of the mixture ferrocenium-oxygen are preserved (Fig. 6). The presence of flexzone does not prevent the formation of the adduct **1g** but avoids its irreversible rearrangement (cf. 3.2.2).

3.2. Decomposition of ferrocenium cations

3.2.1. Decomposition in DMF or DMSO

The experimental results show that an oxidation of DMF or DMSO occurs during the chemical transformation of ferrocenium cations under oxygen. Firstly, in the absence of electrolysis, we observed a partial reduction (50%) of ferrocenium cations into ferrocene in oxygen saturated solutions of DMF or DMSO, secondly, CO₂ was produced during macroscale electrolyses of ferrocene in DMF in the presence of oxygen. Except for ferrocene, the only oxidizable species is the solvent and only DMF can be a source of CO₂. It is worth noting that CO₂ is not obtained during decomposition of ferrocenium cations in DMF without electrolysis. Consequently, as observed by an increase of the anodic peak in cyclic voltammetry (cf. 2.1.1), a second electrochemical process takes place next to the first one which corresponds to the oxidation of starting ferrocene. The second electrochemical process can result both from an oxidation of ferrocene partially produced from chemical transformation of ferrocenium cations as observed in solution and probably from an oxidation of an intermediate giving the unstable *N,N*-dimethyl carbamic acid, (CH₃)₂NCO₂H, which decomposes with CO₂ formation.



Scheme 7.

In order to account all the experimental results, we can propose the mechanism outlined in Scheme 8. The reactions 1–7 occur during the electrochemical oxidation of ferrocene in oxygen-saturated solution of DMF. The reactions 2–5 correspond to the chemical transformation of ferrocenium cations in DMF under oxygen.

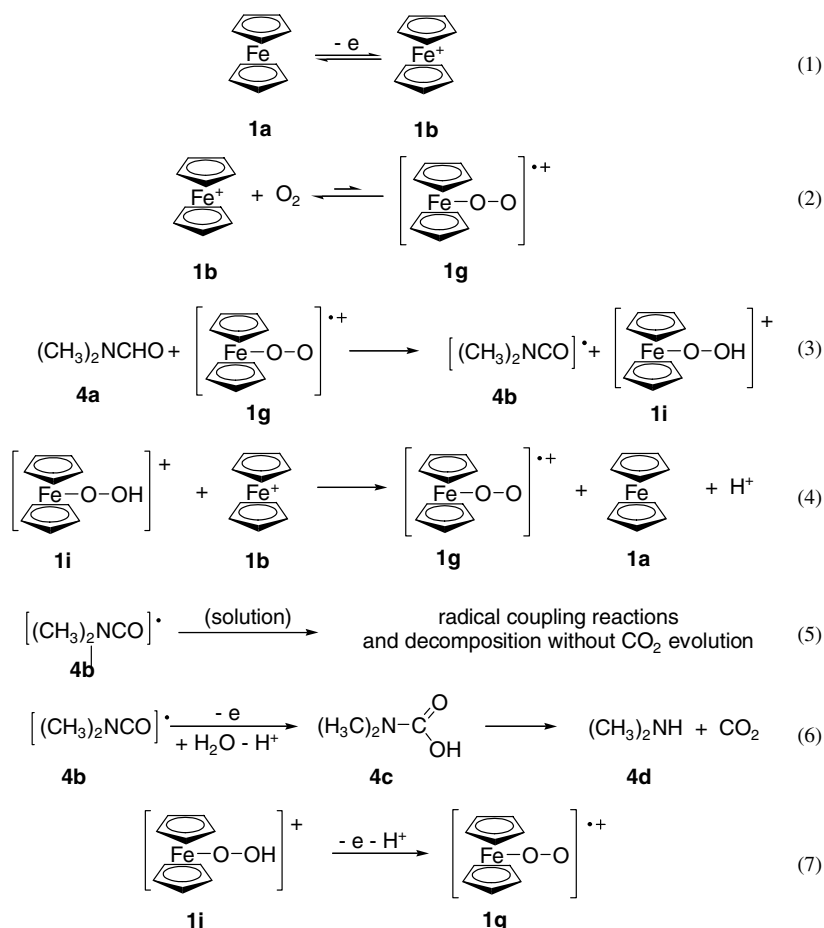
It is well known [21] that hydrogen atom can be transferred from a substrate to a peroxy radical. In this way, the peroxy radical cation **1g** abstracts an hydrogen atom from DMF affording the new radical **4b** and the hydroperoxy cation **1i** (reaction 3). This reaction can take place partly at the electrode during electrolysis, thus, **4b** can be oxidized at the anode giving a cation which adds residual water from the medium producing the unstable hydroxamic acid **4c** (reaction 6). The other part of **4b** produced in solution can give subsequent chemical reactions (radical coupling reactions with **1g**) with decomposition without CO₂ formation (reaction 5). Consequently, about 45% of **4b** are directly oxidized at the anode during macroscale electrolyses and the other part chemically reacts. By analogy with the oxidation of hydroxyperoxide by metal ions [21], a redox reaction (reaction 4) between hydroperoxy cation **1i** and

ferrocenium cation **1b** affords ferrocene **1a** and peroxy radical cation **1g**. The part of hydroperoxy cation **1i** produced at the anode surface according to the reaction 3 may be also electrochemically oxidized (reaction 7). The faradic result (2F per mol of ferrocene) is in accordance with the Scheme 8. Furthermore, an hydrogen atom transfer from *N,N*-dimethylamine **4d** to peroxy radical cation **1g** is conceivable leading to a new aminyl radical and hydroperoxy cation **1i**. The cathodic irreversible peak observed at $-0.45 \text{ V}_{\text{SCE}}$ on the cyclic voltammogram (cf. 2.1.1) can result from reduction of peroxidic species.

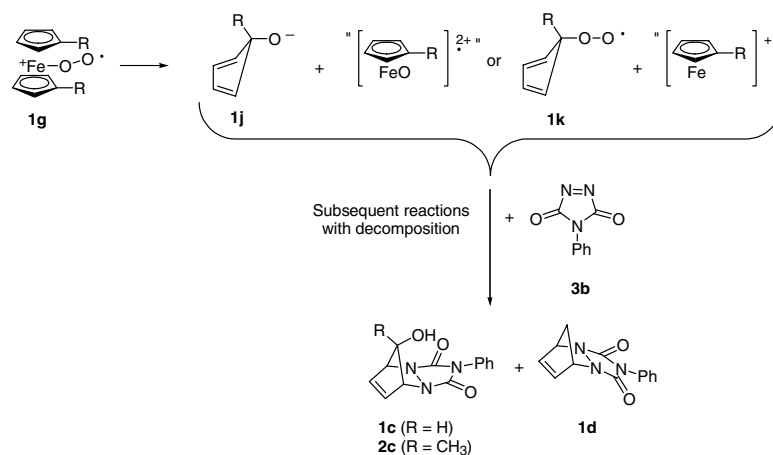
The formation of ferrocene in 50% yield during chemical evolution of ferrocenium cations in oxygen-saturated solution of DMSO probably involves also hydroperoxy cation **1i** as intermediate. DMSO is well known as a H-atom donating solvent.

3.2.2. Decomposition in acetonitrile, acetone or methylene chloride

The trapping with a strong dienophile of cyclopentadien-5-ol in high yields during decomposition of ferrocenium cations in acetonitrile under oxygen necessary



Scheme 8.



Scheme 9.

implies an irreversible oxygen transfer from iron of **1g** to a cyclopentadienyl ligand as shown in Scheme 9. A nucleophilic attack of residual water in basic media cannot be retained. Firstly, the addition of methanol to the solution before the decomposition did not give methoxylated adduct, secondly, the regio (for dimethylferrocenium cations) and stereoselectivity of the reaction are in accordance with an oxygen transfer from central iron (endo addition). A direct reaction of molecular oxygen at cyclopentadienyl ring would probably afford an exo addition. A decomposition in the presence of $^{18}\text{O}_2$ would give an unambiguous answer about the origin of oxygen. The transfer can involve either one oxygen atom with breaking of the O–O peroxy bond, directly affording alcoolate of cyclopentadienol **1j** or the peroxy group giving an unstable peroxy compound **1k**. The presence of an active antioxidant (flexzone) does not avoid the formation of the peroxy radical cation **1g** for which oxidizing properties remain, but inhibits the oxygen transfer to the ligand.

Elemental analyses (cf. 2.3.2.1) of solids isolated from the oxygen decomposition of ferrocenium cations in acetonitrile or methylene chloride is in accordance with a new organometallic iron cation having an organic ligand (probably equivalent to one cyclopentadienyl) with BF_4^- as counter-ion (or ClO_4^- when Bu_4NClO_4 is used as electrolyte). The observed difference of Fe/F ratio higher in acetonitrile than in methylene chloride can be explained by the presence in the former one of a most important part of ferrate ions (FeO_4^{2-}) next to BF_4^- as counterion. Ferrate ions can be produced from complete decomposition of ferrocenium cations. The small amount (12–15%) of adduct between dienophile and cyclopentadiene must correspond to this complete decomposition of ferrocenium cations. After dissolving solids in aqueous acidic medium, ferric ions probably result both from ferrate anions and decomposition of the new organometallic compound. These results are par-

tially in contradiction with the assertion of Zotti et al. [7] who did not consider the presence of a counter-anion in the solid isolated after decomposition.

The simultaneous disappearance of ferrocene and ferrocenium cations in oxygen saturated solution of acetonitrile must involve oxidizing intermediates of decomposition acting with ferrocene.

4. Conclusion

In polar organic solvents, ferrocenium cations are very sensitive to molecular oxygen with which they reversibly form peroxy radical cations. Chemical transformations of these peroxy compounds change according to the nature of the solvent and the presence or not of various substrates in solution. Transformation rates are higher in an oxidizable solvent as DMF or DMSO than in a non-oxidizable one as acetonitrile, acetone or methylene chloride with a complete decomposition in the latter solvents and formation of ferrocene in 50% yield in the former one. In the presence of oxidizable reagents, whatever the solvent, the rates are notably decreased; redox reactions can take place with ferrocene formation without decomposition. Ferrocenium cations in oxygen-saturated solution of polar solvents can be stabilized for a long time at room temperature, by adding active antioxidants in small amounts (molar ratio <5%), but with preserving the oxidizing properties of peroxy radical cation. In conclusion, our study shows that it is necessary to use deaerated solutions even for anodic or chemical oxidations, particularly when the generated species are paramagnetic. Moreover, ferrocene has been currently used as an internal standard for electrochemical measurements [22] and then, in this case, oxygen must be completely eliminated. Because sufficient methyl substitution of the cyclopentadienyl rings can render ferrocenium stable to oxygen, Baskin

and Kinlen [9] proposed the bis(pentamethylcyclopentadienyl) iron as oxygen-stable reference electrode.

5. Experimental

5.1. Chemical and reagents

Solvents (reagent grade) were used without further purification. Tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) and tetrabutylammonium perchlorate (Bu_4NClO_4) were purchased from Fluka. The former salt was crystallized in a mixture methanol–water in order to eliminate traces of iodide ions and dried. Ferrocene and 1,1'-dimethylferrocene (Aldrich) and other chemical were reagent grade and used as received.

Ferrocenium cations were prepared by stirring ferrocene for 2 h in concentrated sulphuric acid in the presence of air. The resulting blue solution was poured on ice and after extraction with diethyl ether, HPF_6 (40% in water) was added to the aqueous solution, then the solid ferrocenium hexafluorophosphate was filtered, washed with diethyl ether and dried.

5.2. Apparatus and procedure

Conventional electrochemical equipment was used for cyclic voltammetry and voltammetry at a rotating disc electrode (EG & G Princeton Applied Research Model 362 scanning potentiostat with an XY recorder). For both cyclic voltammetry and voltammetry at a rotating disc electrode ($\omega = 2000$ rpm), the working electrode was a disc of glassy carbon (3 mm diameter) or platinum (1 mm diameter). All potentials referred to the saturated calomel electrode (SCE) and were not corrected for the ohmic drop.

Controlled potential electrolyses were performed in a cell [23] equipped with a planar electrode (4 cm diameter), made of glassy carbon or platinum. The cell is adapted to collect gas which could evolve from the electrolyzed solution. The coulometric measurements were determined with a current integrator Tacussel IG5N. Electrolyses under continuous bubbling of oxygen generally involve 2–10 mmol of ferrocene in 150–180 mL of solvent (DMF, DMSO, acetonitrile, acetone or methylene chloride) with Bu_4NBF_4 or Bu_4NClO_4 as electrolyte.

Electrolyses in a flow cell [24] fitted with a porous graphite felt (RVG 4000 Le Carbone Lorraine) anode (5.2 cm diameter, 1.2 cm thickness) located between two counter electrodes were carried out at controlled current intensities calculated from the Faraday's law. The solution of substrates was pumped through the cell from a reservoir.

The chemical evolutions and concentrations of ferrocene, ferrocenium cations and other electroactive species

in oxygenated solution of solvents were monitored by voltammetry at a rotating disc electrode. Analyses were generally performed in 30 mL of organic solvent with Bu_4NBF_4 as electrolyte.

5.3. Anodic oxidation of ferrocene at a planar electrode under oxygen

As a general procedure for non oxidizable solvents, the oxidation at a platinum anode of 0.95 g (5.1 mmol) of ferrocene in 160 mL of acetone containing Bu_4NBF_4 (0.1 M) as electrolyte was performed at 1 V_{SCE} . An oxygen bubbling was continuously maintained during all the electrolysis. After total disappearance of the starting ferrocene and consumption of 0.4 F per mol, 0.9 g of a brown precipitate was filtered. This last one was slightly soluble in water without appearance of Fe^{3+} cations in the resulting solution and soluble in nitric acid with formation of Fe^{3+} characterized by adding SCN^- . Addition of aqueous sodium hydroxide to this acidic solution led to a ferric hydroxide precipitate and a deep red solution which turned orange yellow after acidification.

5.4. Anodic co-oxidation of ferrocenes and 4-phenylurazole at a porous electrode

Co-oxidations at a porous graphite felt anode of ferrocene or 1,1'-dimethylferrocene (4 mmol) and 4-phenyl-1,2,4-triazolidine-3,5-dione (4-phenylurazole) (4, 8 or 12 mmol) were performed in 400 mL of acidified acetonitrile (2% H_2SO_4). The total current intensity calculated from Faraday's law was corresponding to 1 F and 2 F per mol of ferrocene and 4-phenylurazole, respectively. Solid sodium carbonate and molecular oxygen were added to the electrolyzed solution at the outlet of the cell. A complete decomposition of ferrocenium and 1,1'-dimethylferrocenium were observed after respectively one hour and one night. After decomposition and filtration, the solution was evaporated by half under vacuum, then after adding an equivalent volume of water, the resulting solution was concentrated under vacuum. The residue was extracted with methylene chloride. After drying, the organic solvent and the crude reaction products were purified by column chromatography (ether) leading to pure Diels–Alder adducts. Physical characteristics of these products were previously reported in a preliminary communication [8].

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