# ANODIC BEHAVIOUR INVESTIGATION OF (FERROCENYLMETHYL) TRIMETHYLAMMONIUM CATION

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**Résumé:** le sel quaternaire (ferrocenylmethyl)trimethylammonium iodide 4 a été préparé par la réaction d'amminométhylation de ferrocène 1 par le réactif de Mannich suivie par quaternisation avec l'iodure de méthyle. L'amine tertiaire obtenue 3 et son sel quaternaire 4 ont été caractérisé par FTIR, NMR <sup>1</sup>H et <sup>13</sup>C. L'investigation du comportement électrochimique du sel quaternaire 4 par voltamètrie cyclique indique que ce sel présent une oxydation réversible monoélectronique. Cette oxydation est influencée par le groupement aminométhyle introduit au ferrocène. Les mêmes remarques sont observées mêmes à des faibles vitesses de balayage.

**Mots clés :** Ferrocène; voltamètrie cyclique; diméthylaminométhylferrocéne; l'iodure de ferrocènylméthyltriméthyammonium ; RMN; comportement Redox.

#### Abstract

The quaternary ammonium salt (ferrocenylmethyl)trimethylammonium iodide 4 containing an amminomethyl group has been prepared by the amminomethylation of ferrocene 1 with the Mannich reagent followed by quaternisation with iodomethane. The obtained tertiary ammine 3 and its methiodide 4 have been characterized by FTIR, <sup>1</sup>H NMR and <sup>13</sup>C NMR. Their electrochemical behaviours have been investigated by cyclic voltammetry, indicating that the quaternary salt 4 exhibit reversible one-electron oxidations of the ferrocene moiety, which is influenced by the aminomethyl group introduced to the ferrocene centre. The same remakes were observed even at slow scan rates.

Keywords: Ferrocene; cyclic voltammetry; dimethylaminomethylferrocene; ferrocenylmethyltrimethyammonium iodide; NMR; Redox behaviour.

# **1-Introduction**

Due to its high stability and reversible redox characteristics, ferrocene 1 has been extensively used as starting materials in the synthesis of versatile ferrocenyl derivatives[1]. For example, ferrocenyl derivatives of the general formula (Ferrocenylmethyl) trimethylammonium cation 2 are very important



electron-transfer systems for molecular electronics owing to its characteristic redox behaviors[2,3], and they could also be expected to play a key role of an electron chemical probe of the electron-transfer process in biological molecules[4].



(Ferrocenylmethyl)trimethylammonium iodide 4 is an example of above systems, this salt can be used to prepare a wide variety of ferrocene derivatives covalently linked to ferrocenyl fragment which have shown some interesting electrochemical behaviours. Recently, there has been increasing interest in ferrocenyl groups containing one or more heteroatom because of their use in the preparation of a wide range of amides which can produce by cyclization heterocyclicferrocene systems [5-8].

## 2- Results and discussion 2-1- Synthesis

The Mannich aminomethylation of ferrocene 1 to N,N-dimehylaminomethylferrocene 3 can be effected by reaction with formaldehyde and dimethylamine in acetic acid or by using methylene-bis-dimethylamine as the aminomethylating agent. [9].

In this paper we report the synthesis of N,Ndimehylaminomethylferrocene **3** from the reaction of ferrocene **1** and the Mannich reagent methylene-bisdimethylamine in a mixture of acetic and phosphoric acids [10]. The addition of formaldehyde to this system does not permit the use of 2:1 molar ratio of ferrocene:methylene-bis-dimethylamine, and equimolar quantities must be used in practice. This type of reaction proceeds with a variety of compounds containing suitably activated hydrogen atoms, such as acetoacetic ester, phenols, and certain reactive olefins, but no reaction with benzene[10]

The synthesis of the Mannich reagent methylene-bis-dimethylamine is already achieved by the condensation of a 25 % and 37 % aqueous solutions of formaldehyde and dimethylamine respectively.



The tertiary amine **3** is converted to its methiodide **4** by the treatment of a solution of the amine in methanol with an excess of iodomethane.



The proton N.M.R. spectrum of the quaternary salt **4** shows five peaks at  $\delta$  3.26, 4.26, 4.29, 4.56, 4.87 ppm. which respectively correspond to the nine protons of the

three methyl group, the nine protons of the unsubsidised and the substituted cyclopentadinyl ring, and the two methylene group. Figure 1.



Figure 1. <sup>1</sup>H. N.M.R spectrum of (ferrocenylmethyl)trimethylammonium iodide 4 in CDCl<sub>3</sub>

The carbon N.M.R. spectrum also shows five peaks, the first at 52.68 ppm correspond to the three carbons of the trimethyl group. The second at 67.16 which correspond to the carbon of the methylene group and the rest of the peaks at 69.63, 70.71 and 72.29 ppm

which correspond to the ten carbons of the ferrocene. Figure 2.



Figure 2. <sup>13</sup>C. N.M.R spectrum of (ferrocenylmethyl)trimethylammonium iodide 4 in CDCl<sub>3</sub>

The methylene group of the salt (ferrocenylmethyl)trimethylammonium iodide **4** is characterised by its down orientation on the dept. spectrum . also all quaternary carbons are disappeared. Figure 3.



Figure 3. Dept spectrum of (ferrocenylmethyl)trimethylammonium iodide in CDCl<sub>3</sub>

# 2-2- Electrochemical studies

Electrochemical experiments were carried out using a potentiostat type voltalab 32. All experiments were carried out in acetontrile which was dried over  $CaH_2$  and distilled prior to use. Cyclic voltammograms were recorded using an individual cell of 10 ml with a conventional three-electrode system in CH<sub>3</sub>CN containing 0.1 M LiCLO<sub>4</sub>. The electrodes were polished by diamond paste and rinsed copiously by acetone and then by acetonitrile. Working electrode was a disc of glassy carbon (diameter 2 mm) while the counter electrode was a platinum wire, and the reference electrode was a saturated calomel electrode (SCE). Potentials were calibrated against ferrocene. The experiments were carried out under a moisture free nitrogen atmosphere. Cyclic voltammetry was measured for an acetontrile solution of ferrocene and the desired compound  $(10^{-3} \text{ M})$  at scan rates equal to 100; 50; 25; and 10 mv.s<sup>-1</sup>.

The cyclic voltammetry results obtained were collected in figure 4.









**Figure 4.** Cyclic voltammograms of a  $10^{-3}$  M solution of ferrocene **1** and compound **4** in  $10^{-1}$  M KClO<sub>4</sub>/CH<sub>3</sub>CN, (a) and (b) at scan rate of 100 mv.s<sup>-1</sup>; (c) and (d) at scan rates of 100(1); 50(2); 25(3) and 10(4)

Relevant electrochemical data obtained from these experiments are summarized in table 1.

Table 1. Electrochemical data for the oxidation of ferrocene 1 and compound 4 measured at 25 °C in  $10^{-1}$  M LiClO<sub>4</sub>/CH<sub>3</sub>CN .

Compound	Λ	Epaı	$Epa_2$	Epa <sub>3</sub>	Epc <sub>1</sub>	Epc <sub>2</sub>	$Epa_1$ - $Epc_1$	E <sub>1/2</sub>	$I_{\rm pc}/I_{\rm pa}$
Ferroce ne 1	100	354	-	-	274	-	64	314	1.07
	50	348	-	-	284	-	64	316	1.07
	25	338	-	-	274	-	64	306	1.09
	10	336	-	-	272	-	68	304	1.03
Compo und <b>4</b>	100	247	575	1698	8.74	494	81	500	1.08
	50	194	566	-	12	494	72	497	1.2
	25	188	554	-	36	486	68	501	1.2
	10	188	564	-	92	482	62	494	1.1

These studies showed that when ferrocene 1 is scanned at scan rate equal to 100 mv.s<sup>-1</sup> it gives one oxidation peak Epa<sub>1</sub> at 354 mv, and also one reduction peak Epc<sub>1</sub> at 274, these two peaks are attributed to the redox couple  $Cp_2Fe(III)/Cp_2(II)$ . Figure 1a. The same results are obtained even one ferrocene is subjected to a successive scan equal to 20 cycles. The unchanged in shape of the voltammogram of ferrocene under this successive scan means that the compound is electrochemical very stable. The voltammograms obtained at different scan rate from 100 to 10 mv.s<sup>-1</sup> indicate in the first hand that ferrocene kept its reversible character and the intensity of courant increase with the increase of the scan rate.

The voltammograms of (ferrocenylmethyl) trimethylammonium iodide 4, obtained at 100 mv.s<sup>-1</sup>, showed one oxidation peak at 274 mv and one reduction peak at 8.74 mv which are attributed to the ferrocenium/ferrocene couple. The other peaks are attributed to the oxidation and the reduction of  $I_2/I^-$  and the trimethylamine in the molecule. Also the oxidation of this compound appeared to be Nerstian and diffusion controlled. Plots of  $(i_p)_{anod}$  verses the square root of the scan rate  $(v^{1/2})$  were linear. The peak-to peak

separations are, however, significantly greater than the ideal value of 60 mvs<sup>-1</sup> for a fully reversible oneelectron processes. This may be due to a combination of uncompensated solution resistance and slightly slow electron-transfer kinetics. The  $E_{1/2}$  of the studied compound is 500 mv is higher compared to the ferrocene 354 mv. This difference may be explained by the influence of the electron withdrawing of the amminometyl group in the molecule. Other relevant electrochemical data obtained from these experiments are summarized in table 1.

Finally the use of ferrocene 1 as an external or an internal reference is not justified because the  $E_{1/2}$  potential values were not sufficiently far each one from another. This observation may be taken as an advantage using the ferrocenic group as an intermolecular reference to determine electrochemical characteristics of all other amino groups contained in the molecule.

### **3- Conclusion:**

The potential values Epa of the aminomethyl group the molecule existing in of ferrocenylmethyltrimethylammonium iodide 4 appear at potentials more anodic as oxidation peaks which are not systematically reversible. These oxidation peaks of aminomethyl groups may be referenced to the ferrocenic residue existing in the same molecules using it as an intermolecular reference seeing that there is no significant difference between ferrocene and ferrocenic molecule containing other aminomethyl groups. It seems very interesting to note that this compound presents no influences on some electrochemical characteristics even when the ferrocene unit is only separated by one methylene group. This work is in progress in our laboratory.

# 4- Experimental

# 4.1- Methods

All reactions were carried out under an oxygenfree atmosphere. Solutions were dried over anhydrous magnesium sulphate and evaporated under reduced pressure using a rotary evaporator. Solvents were dried by standard methods and distilled prior to use[12].

# 4.2- Chemicals.

All chemicals were of reagent grade, purchased from Aldrich Chemical Co., Sigma Chemical Co., or Fisher Chemical Co. and were used without further purification.

# **4.3- Instrumentation**

<sup>1</sup>H NMR spectra were recorded on a Bruker AC 250 MHz spectrometer and the shifts are reported downfield from tetramethylsilane. The designations Ha, Hb are used for the monosubstituted cyclopentadienyl ring. <sup>13</sup>C NMR spectra were recorded on a Bruker 350 MHz spectrometer. The spectra reported are proton decoupled, and the shifts are reported downfield from tetramethylsilane. Mass spectra were recorded on a triple quadripôle Sciex API III Plus mass spectrometer. IR spectra were recorded on Perkin Elmer 1000-FTIR Specrtrometer using KBr pellets. Melting points were obtained on a Gallenkamp melting point apparatus, and are uncorrected.

## 4.4-Procedures

N,N-dimehylaminomethylferrocene **3** and its methiodide **4** were prepared according to the literature methods [8].

# Dimethylaminomethylferrocene 3

Ferrocene (4.6 g, 0.025 mol) was added to a well stirred solution of methylene-bis-dimethylamine (4.3g, 0.042 mol), phosphoric acid (4.3 g, d, 1.75) and glacial acetic acid (400 cm<sup>3</sup>). The resulting suspension was heated at 100 C° under a slow stream of nitrogen for 5 hours. The cold solution was poured into water (60 cm<sup>3</sup>) and extracted with ether to remove the unreacted ferrocene. The aqueous solution was then cooled in an ice bath and made alkaline with sodium hydroxyde pellets and extracted with ether. The ether extracts were dried and evaporated to yield a thick brown oil of dimethylaminomethylferrocene 5.4 g, yield 90%.

<sup>1</sup>**H R.M.N.** : δ 2.14 (s, 6H, H6); 3.24 (s, 2H, H5); 4.07 (s, 5H, H4) and 4.14 ppm (s, 4H, H2 et H3).

<sup>13</sup>C R.M.N. : δ 44.76 (2C, C6); 59.14 (C, C5); 67.97 (2C, C2 ou C3); 68.43 (5C, C4); 70.04 (2C, C3 ou C2); and 83.15 ppm (1C, C1)

### (ferrocenylmethyl)trimethylammonium iodide 4

To a solution of the tertiary amine dimethylaminomethylferrocene (5.4 g, 0.022 mol) in methanol (6 cm<sup>3</sup>) was iodomethane (6 cm<sup>3</sup>) and the resulting mixture was heated on a steam bath for 10 minutes. The yellow solid was then filtered to yield (ferrocenylmethyl)trimethyl-ammonium iodide (9.3 g, 97%) as a yellow-orange solide, m.p.  $218^{\circ}$ C.

**I.R. (KCl, disc)** 1238.2 ; 1473.5 ; 2399.3 ; 3012.6 et à 3618.2 cm<sup>-1</sup>

<sup>1</sup>**H R.M.N.** : δ 3.26 (s, 9H, H6), 4.26 (s, 5H, H4), 4.29 (s, 2H, H2 ou H3), 4.56 (s, 2H, H3 ou H2) ; and 4.87 ppm (s, 2H, H5)

<sup>13</sup>C R.M.N.: δ 52.68 (9C, C6), 67.16 (2C, C5), 69.63 (5C, C4), 70.71 (2C, C3 ou C2); and 72.29 ppm (2C, C2 ou C3)

Found : C, 44.1 ; H, 5.4 ; N, 3.7. calculated for  $C_{14}H_{20}FeNI$  : C, 43,7 ; H, 5.2; N, 3;6%

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