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Electrochemical and Positron Annihilation Studies of Semicarbazones and Thiosemicarbazones Derived from Ferrocene

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Uma série de seis derivados de ferroceno contendo uma cadeia lateral de semicarbazona ou tiossemicarbazona foi investigada por voltametria cíclica e estudos utilizando medidas de tempo de vida de pósitrons. Ambos os fenômenos, tanto o processo redox como o de captura de elétrons, ocorreram no átomo de ferro. Foram propostas correlações entre os dois métodos, levando em conta os substituintes na cadeia lateral dos compostos, os potenciais redox e as probabilidades de formação de o-positrônio (o-Ps).

A series of six ferrocene derivatives containing a semicarbazone or thiosemicarbazone side chain was investigated by cyclic voltammetry and positron annihilation lifetime measurements. Both the redox and the electron capture processes took place on the Fe atom. Correlations between the two methods were proposed, taking into account the substituents on the side chain of the compounds, their redox potentials and the probabilities of o-positronium (o-Ps).formation.

Keywords: *semicarbazone, thiosemicarbazone, ferrocene, cyclic voltammetry, positronium formation*

Introduction

Positrons can form positronium (Ps) in molecular solids. Interest in the behaviour of the positron-electron (Ps) pair lies in that the probability of its formation (I) and its lifetime (τ) depend upon the physical and chemical properties of the solid[1-3]. However, much more attention has been devoted to studies applied to metals and alloys than to molecular compounds.

Two Ps varieties can be formed: p-Ps (singlet) and o-Ps (triplet), depending on the relative spins of the positron and the electron. Therefore, if Ps formation occurs, the lifetime spectra consist of three exponential components standing for p-Ps ($\tau_1 = 120$ ps), free and bound positrons ($\tau_2 = 150 - 500$ ps) and o-Ps ($\tau_3 > 900$ ps), with the associated formation probabilities, I_1, I_2 and I_3, respectively. Normally one works with the parameter of the longer lived variety, (o-Ps), τ_3 and I_3.

Work on metal complexes is relatively scarce and has only been performed in recent years. Very few examples exist involving metallocenes, which prompted us to investigate the systems described here. Figure 1 shows the structure of the systems under study.
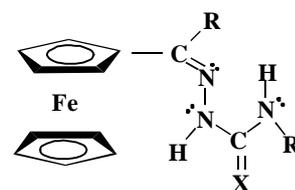
Figure 1. General structure of the compounds studied in this work

Studies concerning complexes of thiosemicarbazones and semicarbazones have been published in the literature[4-7], mostly dealing with their structural and spectroscopic aspects. In the present work cyclic voltammetry and PAL measurements of the ferrocene derivatives was undertaken and the results show that the side chain affects the process taking place on the Fe atom. Since PAL measurements of metal complexes are still very scarce, and experiments on

metallocenes are even scarcer we firmly believe that attempts to correlate this with other physical methods are extremely welcome at this stage.

Experimental

Preparation of the complexes

The ferrocene derivatives used in this work were prepared by literature methods[8-10]:

cpFecp—C(=O)(R) + H_2NNH—C(X)(NHR') $\xrightarrow[\text{reflux, EtOH / H}_2\text{O, 2 h}]{\text{NaOAc (X = O), HOAc (X = S)}}$

R = H, CH₃   R' = H, Ph

cpFecp—C(R)=N—NH—C(X)—NHR' + H_2O
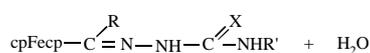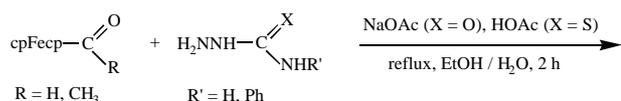
Six different products were obtained, with yields ranging from 51 to 90%. They were characterised satisfactorily by elemental analysis, m.p. and ^1H and ^{13}C NMR spectroscopy. All the results conformed to the literature. Table 1 lists all six compounds.

Cyclic voltammetry

Cyclic voltammetry experiments were performed using a model 273A EG/PARC potentiostat/galvanostat, connected via a GPIB interface with a computer provided with the M270 EG/PARC electrochemical software. Determinations were carried out in MeCN, using a Pt working electrode, an Ag/AgCl reference electrode and Bu_4NClO_4 as the supporting electrolyte.

Positron annihilation lifetime (PAL) measurements

The positron lifetime is measured experimentally as the time delay between the 1.28 MeV γ ray emitted by the

^{22}Na radionuclide immediately after the positron emission, and the 0.5 MeV annihilation radiation. This can be done using a conventional "fast-fast" coincidence system. Our measurements employed such a system (ORTEC), with a time resolution of 280 ps, given by a ^{60}Co prompt curve. The ^{22}Na positron source with ca. 4.0 x 10^5 Bq activity was sandwiched between two identical 3.5 μm thick Mylar foils. The source correction was approximately 10%. All the experiments were carried out at 294K under atmospheric pressure. The experimental apparatus has already been described elsewhere[11].

The time resolution of the apparatus (280 ps) makes the data on the shortest-lived component, ascribed to p-Ps, somewhat unreliable. In order to reduce the scattering of the other parameters, the value of τ_1 was fixed at 120 ps, near the intrinsic value of 125 ps of p-Ps *in vacuo*[12]. On this basis the quality of the fit of the spectra (e.g. its reduced chi-square and the corresponding excess of probability) is not significantly altered and the derived parameters are close to those obtained when the analysis is made without any retraints.

The experimental errors for the PAL parameters τ_3 and I_3, determined over multiple measurements, were found to be 50 ps and 1.0%, respectively.

Results and Discussion

A recent work [13] showed that the electronic configuration of the central atom in coordination compounds or in metallocenes is of paramount importance in Ps formation. Metal complexes can be divided into 2 classes in this respect: class 1, in which Ps formation is observed in appreciable amounts and the metal presents completely filled 3d or 4d orbitals; class 2, whose metals have incompletely filled 3d or 4d orbitals, giving very low I_3 values. When the e^*_{1g} frontier orbital is occupied, as in cobaltocene (19 electrons) or nickelocene (20 electrons), oxidation of the species can occur, leading to cationic species which are strong inhibitors

Table 1. Cyclic Voltammetry and o-Ps formation data

Compound	R	R'	X	E_{pa} (V)	E_{pc} (V)	$E_{1/2}$ (V)	τ_3 (ns)	I_3 (%)
HFFS **1**	H	H	O	0.49	0.42	0.46	1.48	13.6
HAFS **2**	Me	H	O	0.48	0.41	0.45	1.37	25.6
HFFT **3**	H	H	S	0.57	0.50	0.53	1.56	5.9
HAFT **4**	Me	H	S	0.52	0.44	0.48	1.29	16.9
HFFT **5**	H	Ph	S	0.57	0.51	0.54	1.64	16.6
HFAT **6**	Me	Ph	S	0.50	0.42	0.46	1.63	11.3
1 + HClO₄				0.69	0.57	0.63		
2 + HClO₄				0.71	0.62	0.67		
3 + HClO₄				0.62	0.54	0.58		
4 + HClO₄				0.68	0.59	0.64		
5 + HClO₄				0.63	0.57	0.60		
6 + HClO₄				0.68	0.58	0.63		

HFFS = formylferrocenesemicarbazone; HAFS = acetylferrocenesemicarbazone; HFFT = formylferrocenethiosemicarbazone; HAFT = acetylferrocenethiosemicarbazone; HFFT = formylferrocenethiosemicarbazone; HAFT = acetylferrocene-thiosemicarbazone

of Ps formation. This is the likely reason for the absence of Ps formation in cp_2Co and cp_2Ni. Ferrocene, on the other hand, forms Ps. We are here presenting evidence of the dependence of Ps formation on factors that alter the electron density on the Fe atom, and that some relationship can be drawn with cyclic voltammetric data. If ferrocene is considered a d^6 Fe^{2+} species, as in the traditional ligand field treatment, with the ligands in the cp^- form, and an appreciable ionic character in its formulation, no Ps formation is to be expected. Considering, however, a molecular orbital treatment in which the iron atom is the centre of an 18 electron system, one can expect P_s formation. The present work shows for the first time evidence of P/s formation in ferrocene derivatives, up to quite an appreciable degree, such as in compound **2** (Table 1).

The reversible oxidation processes of the ferrocene derivatives always occur on the metal atom. Table 1 shows that the thiosemicarbazone species (compounds **3** to **6**) are oxidized at higher potentials than the corresponding semicarbazone complexes (compounds **1** and **2**). This means that the sulphur-bearing chains cause Fe to be electron poorer, hence its greater difficulty to be oxidized. For each complex the addition of $HClO_4$ increases the oxidation potential, *i.e.*, it produces an effect similar to that described above, when the S- and O-containing chains were compared. In the present case protonation of the side chain contributes to increase its demand for electrons, and as a consequence the available electron density on the Fe atom is lowered. The value of the oxidation potential of the Fe^{2+} ion is sensitive to a variation in the group attached to the carbon adjacent to the cyclopentadienyl ring. In all cases, when one goes from $C-CH_3$ to C-H the oxidation potential increases. H is more electronegative than CH_3, as shown by the strengths of formic and acetic acids. The change from $C-CH_3$ to H thus corresponds to a withdrawal of electron density from the side chain, which is reflected in lower electron availability on the Fe^{2+} ion.

The different groups attached to the amide nitrogens do not play any significant influence on the oxidation potentials of Fe^{2+}. They are far too removed from the metal and are not capable of causing any detectable change. Thus, comparison between **3** and **5**, as well as between **4** and **6** does not show any variation within each pair.

Looking at Table 1, one sees that it is easier to oxidize Fe^{2+} (lower $E_{1/2}$ values) when X = O than when X = S. This means that, when X = O there is less electron density available to the ferrocene moiety from the side chain. The opposite occurs when the compounds are acidified with $HClO_4$, *i.e.*, $E_{1/2}$ is lower when X = S than when X = O.

In the first case, *i.e.*, in the absence of acid, one can draw a resonance structure as shown in Figure 2, in which a negative charge can be ascribed to the oxygen atom and to the carbon atom next to the cyclopentadienyl ring. The oxygen atom,

being more electronegative, will stabilize this structure to a greater extent than sulphur. In addition, the latter will be part of a tautomeric compound, one of whose forms will present an SH group. Of course this tautomeric form will not stabilize the negative charge. Therefore the semicarbazones will be more effective in making more electron density available to the ferrocene moiety than the thiosemicarbazones.
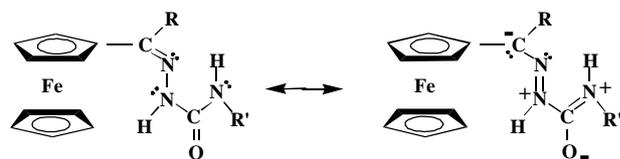
Figure 2. Resonance structures of a ferrocene semicarbazone.

When $HClO_4$ is added to the compounds all $E_{1/2}$ values increase, although the situation regarding the two sets of compounds is inverted, and it becomes relatively easier to oxidize the thiosemicarbazones than the semicarbazones. The latter will protonate better than their sulphur analogues, making electron density less available for the ferrocene moiety.

Table 1 also presents the PAL measurement results. The important data are those given by I_3, since τ_3 usually does not show any significant differences.

It is noteworthy that an increase in electron density on the Fe atom leads to an increase in the probability of Ps formation. Indeed, comparing compounds **1** ($I_3 = 13.6$ %) and **2** ($I_3 = 25.6$ %), the replacement of an H atom by a CH_3 group on the carbon closest to the ring increases the intensity of Ps formation, and the same is true of the pair **3** ($I_3 = 5.9$ %) and **4** ($I_3 = 16.9$ %). Previous results have shown that Ps formation is favoured by an increase in electron localization due to an inductive effect. As an example, the hardening of the metal centres on changing their oxidation state from 0 in $[Pd(PPh_3)_4]$ to $2+$ in $[PdCl_2(PPh_3)_2]$ may explain the absence of Ps formation in the latter compound[12]. The behaviour shown by our two pairs above can be explained in a similar manner.

In the last pair of compounds (**5** and **6**), although the trends observed in the electrochemical experiments still prevailed, the Ps data did not provide any clear distinction. It seems that the presence of the phenyl group interferes with Ps formation at the metal centre, and does not lead to the expected increase in I_3 from **5** to **6**, but rather to a small decrease. It must be bourne in mind that the cyclic voltammetric experiments were performed in solution, whereas PAL measurements were carried out in solid samples. Thus, the compounds containing the phenyl groups (*i.e.*, with an NHPh chain ending) may present intermolecular effects in the solid state which differ from those exhibited

by the other compounds (with an NH_2 end group). Nevertheless, in spite of the difficulties presented by the **5-6** pair, this work showed for the first time that comparative results can be obtained from such different methods as cyclic voltammetry and positron annihilation studies. It is hoped that future work will probe these connections still further.

Acknowledgements

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