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DECOMPOSITION OF THE FERRICENIUM CATION BY NUCLEOPHILIC REAGENTS

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SUMMARY

ESR, electronic absorption and susceptibility measurements have demonstrated that, whereas the ferricenium cation $FeCp_2^+$ is stable in acetonitrile, acetone and nitromethane, it is decomposed by Cl^- and Br^- to $FeCp_2$ and FeX_4^- and by DMF, DMSO, HMPTA, *o*-Phen and Bipy to $FeCp_2$ and an Fe^{II} complex, octahedrally coordinated by the added donor molecules. These results are explained by a reaction mechanism in which the primary step consists of ligand exchange around the Fe^{III} ion. The $C_5H_5^-$ ions which separate have a high reducing power, and so reduction of $FeCp_2^+$ and the Fe^{III} complex formed takes place in secondary reactions. Because of the coupling of the ligand exchange reaction to the reduction reactions and the irreversible transformation of C_5H_5 radicals, even donors that are much weaker than $C_5H_5^-$ can decompose $FeCp_2^+$.

Iodide ions were found to reduce $FeCp_2^+$ to $FeCp_2$. This and other differences between the I^- ions and the Cl^- and Br^- ions are caused by the weaker donor strength of I^-, its higher reducing power and its tendency to associate with I_2 to I_3^- anions.

INTRODUCTION

Ferrocene and its derivatives are stable under many conditions. Under oxidative conditions, however, they become unstable. Even in the initial studies on the oxidation of ferrocene ($FeCp_2$) this instability was related to the decomposition of the ferricenium cation ($FeCp_2^+$)[1]. The nature of the decomposition products and of the decomposition reaction was not established, however. Later on, Riemschneider and Helm[2] and Nesmeyanov and co-workers[3] found that in the oxidation of $FeCp_2$ by chlorine or bromine in organic solvents the reaction products depend on the reaction conditions. At low temperatures ferricenium perhalides are formed, at intermediate temperatures ferricenium tetrahaloferrates, and at high temperatures complete destruction to ferric halides takes place. Similar observations have since been made by others[4,5]. In an attempt to record the ESR spectrum of the $FeCp_2^+$ cation Golding and Orgel[6] observed that halide ions destroy the $FeCp_2^+$ ion and they suggested that tetrahaloferrates are formed. This partly explains the results of Nesmeyanov *et al.*[3].

In the course of our study of the ESR spectrum of the ferricenium cation[7] we also observed that the $FeCp_2^+$ ion is rather unstable. Many nucleophilic reagents were found to decompose $FeCp_2^+$ into ferric or ferro complexes. The apparent lability of $FeCp_2^+$ to attack by various donor molecules seems to indicate that the bonding between the cyclopentadienyl anion Cp^- and the Fe^{3+} cation in $FeCp_2^+$ is rather weak. This, however, is in contradiction with recent crystallographic studies[8,9] which show that the iron-ligand distance in $FeCp_2^+$ is not much different from that in $FeCp_2$, and the bonding between Cp^- and Fe^{2+} in $FeCp_2$ is known to be strong. To find the reason for this discrepancy we have investigated the behaviour of $FeCp_2^+$ towards many nucleophilic agents.

RESULTS

In this section we describe how, by using a combination of spectroscopic techniques, we established which products are obtained when adding donor ligands or solvents to ferricenium salts. It will be shown that with different types of donors different products are obtained. The experimental results will be presented in four groups, according to the reaction products formed. In the subsequent section we discuss the possible reaction schemes leading to these reaction products, and show that, although four types of reactions can be distinguished, all the reaction products can be rationalized by one and the same set of ligand exchange and reduction–oxidation equilibria, followed by an irreversible transformation of Cp radicals.

(*i*) *Decomposition by Cl^- and Br^-*

When tetra-n-butylammonium chloride is added to a green solution of ferricenium picrate in acetone, the colour immediately changes to red-brown for concentrated solutions and yellow for dilute solutions. ESR and electronic absorption measurements show that the spectra characteristic of the $FeCp_2^+$ cation[7] have vanished and that new spectra, characteristic of the $FeCl_4^-$ ion, have appeared. So, in solid solution at 20° and 77°K and in liquid solution at 295°K the new ESR spectrum consists of a symmetric line at $g=2.01$. This spectrum is identical in all respects to those of a solution of $FeCp_2^+ \cdot FeCl_4^-$ in acetone and of a solution of $FeCl_3$ and tetra-n-butylammonium chloride in acetone. From studies by Drago *et al.*[10] and others[11], it is known that in the latter case the $FeCl_4^-$ anion is present in solution. The electronic absorption spectrum of a solution of $FeCp_2^+ \cdot BF_4^-$ and a fivefold excess of $R_4N^+ \cdot Cl^-$ in acetonitrile is presented in Fig. 1. This spectrum is identical to that of $FeCl_4^-$ as measured by several authors[10–12], and confirms the ESR results.

Quantitative UV measurements revealed that the $FeCl_4^-$ formed only accounts for one third of the $FeCp_2^+$ decomposed. This indicates that along with $FeCl_4^-$, at least one other iron compound must be formed after addition of Cl^- ions to $FeCp_2^+$. By two independent experiments we have shown that ferrocene is in fact, formed. In the first place we measured the susceptibility of the $FeCp_2^+$ solution before and after Cl^- addition. We found an increase of the paramagnetic bulk shift of the internal reference TMS proton line after addition of Cl^-. This increase is satisfactorily accounted for by the $FeCl_4^-$ ions, and indicates that the other iron compound formed by decomposition of $FeCp_2^+$ must be diamagnetic. The only possible compound is ferrocene.

We have confirmed this conclusion with the aid of UV absorption experiments.

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In the course of our study of the ESR spectrum of the ferricenium cation[7] the complex $FeCl_2S_4^+$ is formed[10,14], where S is a solvent molecule. Comparison of the intensity ratio of the 360 and 310 nm bands in our absorption spectrum of a decomposed solution ($FeCp_2^+/Cl^- = 1/1$) with results published by Drago *et al.*[10] shows that $FeCl_2S_4^+$ has indeed been formed in addition to $FeCl_4^-$. The signal at $g = 4.4$ which is at the same time observed in the ESR spectrum at 20° and 77°K, in addition to the $FeCl_4^-$ signal at $g = 2.01$, is in accord with this, since this signal can be ascribed to an Fe^{III} complex with a large zero field splitting[15], such as $FeCl_2S_4^+$ should have. Since both $FeCl_4^-$ and $FeCl_2S_4^+$ absorb in the 360–310 nm region, a quantitative determination of $FeCl_4^-$ is difficult. The figures given in the fifth column of Table 1 for $(Cl^-) < (FeCp_2^+)$ should therefore be considered as order of magnitude estimates.

In the reaction of ferricenium salts with tetra-n-butylammonium bromide in acetone, nitromethane, or acetonitrile, results have been obtained which are analogous to those with $R_4N^+ \cdot Cl^-$. Thus addition of $R_4N^+ \cdot Br^-$ changed the colour of a $FeCp_2^+$ solution to brown, while the ESR spectrum of $FeCp_2^+$ vanished and a new spectrum appeared. This spectrum was identical with that of a mixed solution of $FeBr_3$ and $R_4N^+ \cdot Br^-$. The visible and near-UV spectrum[12] confirmed the presence of $FeBr_4^-$, and furthermore demonstrated that only one third of the $FeCp_2^+$ cations decompose into $FeBr_4^-$. The indirect absorption experiment described above proved that $FeCp_2$ is also formed and that it accounts for the remainder of the decomposed $FeCp_2^+$. Within the uncertainties of the experiments the quantitative absorption measurements gave results identical to those obtained with $R_4N^+ \cdot Cl^-$ (*cf.* Table 1). So for both $X^- = Cl^-$ and $X^- = Br^-$ the decomposition reaction is:

$$3\,FeCp_2^+ + 4\,X^- \rightarrow 2\,FeCp_2 + FeX_4^- + 2\,Cp$$

TABLE 1

RELATIVE CONCENTRATIONS OF COMPOUNDS BEFORE AND AFTER ADDITION OF Cl^- TO A SOLUTION OF $FeCp_2^+ \cdot BF_4^-$ IN ACETONITRILE

Before		*After*		
$FeCp_2^+$	*Cl^-*	*$FeCp_2^+$*	*$FeCp_2$*	*$FeCl_4^-$*
3.3	20	0.0	2.3	1.0
3.3	5	0.0	2.1	1.0
3.3	2.5	1.0	1.1	(1.0)
3.3	1.25	2.3	0.5	(0.6)

(*ii*) *Decomposition by other strong donors*

Ferricenium salts decompose rapidly in DMSO and HMPTA and somewhat slower in DMF*. Absorption measurements show that ferrocene is formed and that it accounts for half of the decomposed $FeCp_2^+$. This suggests that in these solvents the decomposition reaction is:

$$2\,FeCp_2^+ + 6\,S \rightarrow FeCp_2 + FeS_6^{2+} + 2\,Cp$$

where S is a solvent molecule. Because of the very low extinction coefficient of the

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* This slower reaction enabled us in previous studies[7] to measure the ESR spectrum of $FeCp_2^+$ in DMF by quickly freezing the solution after addition of the $FeCp_2^+$ salt to DMF.

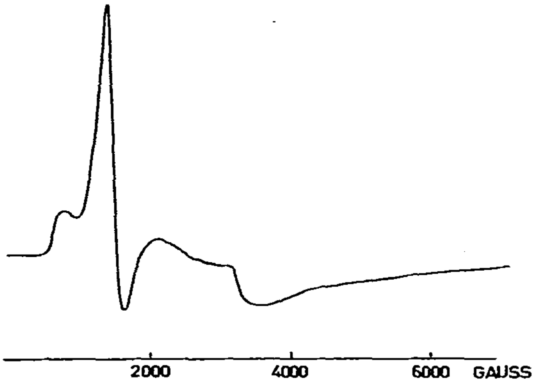

Fig. 2. ESR spectrum of a solution of ferricenium picrate in DMSO at 20°K. Modulation 100 kHz, 5 G; microwave frequency 9150 MHz.

$\mathrm{FeS_6^{2+}}$ complexes in the visible and near-UV region, absorption measurements could not be used to measure the concentration of these complexes.

Other measurements, however, are not in contradiction with the proposed reaction scheme. Thus the measured susceptibility shift of the TMS proton line is too small for a total conversion of $\mathrm{FeCp_2^+}$ into $\mathrm{Fe^{II}}$ or $\mathrm{Fe^{III}}$. Furthermore, although after addition of $\mathrm{FeCp_2^+}$ salts to DMSO, HMPTA or DMF an ESR signal can be measured (Fig. 2), it is much too weak to account for half of the decomposed $\mathrm{FeCp_2^+}$. This ESR signal, which is characteristic of an $\mathrm{Fe^{III}}$ complex with a large zero-field splitting[15], probably belongs to a complex of the type $\mathrm{FeS_6^{3+}}$ or $\mathrm{FeS_5A^{2+}}$, where S is a solvent molecule and $\mathrm{A^-}$ an anion present in solution[10]. Such complexes may have been formed in small amounts by oxidation of the analogous $\mathrm{Fe^{II}}$ complexes.

With 2,2'-bipyridine and *o*-phenanthroline, also, we found that ferrocene and $\mathrm{Fe^{II}}$ complexes are formed:

$$2\,\mathrm{FeCp_2^+} + 3\,\mathrm{Phen} \rightarrow \mathrm{FeCp_2} + \mathrm{Fe(Phen)_3^{2+}} + 2\,\mathrm{Cp}$$

Thus when 2,2'-bipyridine or *o*-phenanthroline are added to solutions of $\mathrm{FeCp_2^+}$ in acetonitrile, the red-violet colour of $\mathrm{Fe(Bipy)_3^{2+}}$ and $\mathrm{Fe(Phen)_3^{2+}}$ immediately develops, and quantitative absorption measurements show that these compounds account for half of the $\mathrm{FeCp_2^+}$ decomposed.

(*iii*) *Interaction with weak donors*

All $\mathrm{FeCp_2^+}$ salts were found to be stable—at least for a few hours—in acetone, nitromethane and acetonitrile. Furthermore tetraalkylammonium tetrafluoroborate, nitrate and perchlorate did not give any reaction with $\mathrm{FeCp_2^+}$ salts, as shown by the unchanged ESR and absorption spectra.

(*iv*) *Reduction by* I^-

On addition of tetra-n-butylammonium iodide to a solution of ferricenium picrate in acetone the colour changes to brown, and ESR measurements indicate that the $\mathrm{FeCp_2^+}$ cations have disappeared. No new ESR signals are recorded, either at room temperature in liquid solution or at 77° and 20°K in solid solution. This suggests that the $\mathrm{FeCp_2^+}$ cations are transformed into diamagnetic molecules or into $\mathrm{Fe^{II}}$

TABLE 2

RELATIVE CONCENTRATIONS OF COMPOUNDS BEFORE AND AFTER ADDITION OF I^- TO A SOLUTION OF $FeCp_2^+ \cdot BF_4^-$ IN ACETONITRILE

Before		*After*	
$FeCp_2^+$	*I^-*	*$FeCp_2^+$*	*$FeCp_2$*
3.3	20	0.0	3.3
3.3	5	0.0	3.3
3.3	2.5	0.7	2.7
3.3	1.25	2.2	1.2

complexes. Evidently no FeI_4^- is formed in contrast to the results with chloride and bromide. This is in accord with the fact that FeI_4^- is unstable to autoreduction of the metal ion in solution at room temperature[16]. Susceptibility measurements show that after addition of $R_4N^+ \cdot I^-$ the resulting solution is diamagnetic. Since $FeCp_2$ bands in the absorption spectrum will be hidden under I_2 and I_3^- bands, we have shown that $FeCp_2^+$ is completely converted into $FeCp_2$ after addition of $R_4N^+ \cdot I^-$ by reoxidizing $FeCp_2$ with an aqueous $FeCl_3$ solution and measuring the resulting $FeCp_2^+$ 615 nm absorption band. The quantitative results are presented in Table 2. They reveal that the following reduction takes place:

$$2\,FeCp_2^+ + 2\,I^- \longrightarrow 2\,FeCp_2 + I_2$$

DISCUSSION

The experimental results in cases (*i*), (*ii*) and (*iii*) can be explained by assuming that in a primary step ligand exchange around the Fe^{III} ion occurs:

$$FeCp_2^+ + n\,L \rightleftarrows FeL_n^{3+} + 2\,Cp^- \quad (1)$$

In this reaction L can be a solvent molecule, a neutral nucleophilic agent or a mononegative anion. The FeL_n^{3+} complex can be a tetrahedral complex such as FeX_4^- or an octahedrally coordinated FeL_6^{3+} (L being monodentate) or FeL_3^{3+} (L being bidentate) complex. Because of the high reducing power of the generated Cp^- anions, reduction of Fe^{III} complexes present in solution will take place:

$$Cp^- + FeCp_2^+ \rightleftarrows Cp + FeCp_2 \quad (2a)$$

$$Cp^- + FeL_n^{3+} \rightleftarrows Cp + FeL_n^{2+} \quad (2b)$$

In subsequent reactions the resulting cyclopentadienyl radicals Cp will combine to Cp_2 or abstract hydrogen atoms from solvent molecules to form cyclopentadiene, which in turn will dimerize to $C_{10}H_{12}$:

$$2\,C_5H_5 \rightarrow C_{10}H_{10} \text{ or } C_{10}H_{12} \quad (3)$$

Reaction (1) explains why the stronger donors decompose the $FeCp_2^+$ cation, whereas no reaction is observed with weak donors (according to Gutmann[17] the donor strength increases in the series nitromethane $< I^- <$ acetonitrile $<$ acetone $< H_2O <$ $Br^- <$ DMF $\sim Cl^- <$ DMSO $<$ HMPTA). For the stronger donors the position of the ligand exchange equilibrium (1) lies to the right, while for weak donors it lies to the left. Because of the subsequent reactions (2) and (3), however, there is no fair competition between the L and Cp^- ligands for the Fe^{III} ion. The fact that a donor like DMF decomposes $FeCp_2^+$, whereas acetone does not, does not therefore imply that the donor strength of Cp^- towards Fe^{III} is intermediate between those of DMF and acetone. In fact, since both equilibria lie far to the right, it means that the donor strength of Cp^- must be considerably greater than that of the weakest donor capable of decomposing $FeCp_2^+$. On chemical grounds it is not surprising that the Cp^- anion should be a strong donor.

In the light of the above explanation, the stability of $FeCp_2^+$ in (acid) aqueous solution[1] and its decomposition in alkaline aqueous solution[18] is understandable, for one would expect the donor strength of water to be insufficient for decomposition of $FeCp_2^+$, whereas the donor strength of OH^- suffices.

Reactions (2a) and (2b) explain why with different agents different products are obtained [*cf.* results (*i*) and (*ii*)]. Since in reaction (1) two Cp^- anions are formed for every FeL_n^{3+} ion, at least one $FeCp_2^+$ cation will be reduced to $FeCp_2$. Which other iron complex will be reduced depends on the difference between the redox potentials of the couples $FeCp_2$–$FeCp_2^+$ and FeL_n^{2+}–FeL_n^{3+} and consequently on the equilibrium constant of the reaction (2c). If equilibrium (2c) is to the left, then the total

$$FeL_n^{3+} + FeCp_2 \rightleftarrows FeL_n^{2+} + FeCp_2^+ \tag{2c}$$

decomposition* reaction of $FeCp_2^+$ will be

$$3\,FeCp_2^+ + n\,L \rightarrow FeL_n^{3+} + 2\,FeCp_2 + 2\,Cp$$

Apparently this is the case for $L = Cl^-$ and $L = Br^-$ (with $n = 4$). We confirmed this for $L = Cl^-$ by observing that $R_4N^+ \cdot FeCl_4^-$ and $FeCp_2$ in acetonitrile do not give a reaction. On the other hand, if equilibrium (2c) is to the right, then the overall decomposition is

$$2\,FeCp_2^+ + n\,L \rightarrow FeL_n^{2+} + FeCp_2 + 2\,Cp$$

This is the case for L=DMF, DMSO, HMPTA, Bipy and Phen.

In relation to the foregoing we should mention some results which puzzled us at first, and which show how careful one must be in extrapolating from well-known facts relating to hexa-aquo iron complexes in aqueous solution to other iron complexes in non-aqueous solutions. In the initial stage of the investigation we used *o*-phenanthroline for the detection of Fe^{II} compounds resulting from decomposition of $FeCp_2^+$ by nucleophilic agents. However, quantitative evaluation of the data nearly always led to strange results. Our later finding that *o*-phenanthroline decomposes $FeCp_2^+$ explains this. For, in addition to the reaction of Phen with Fe^{II}, in which $Fe(Phen)_3^{2+}$ is formed directly, there is also a reaction between $FeCp_2^+$ and Phen and a reaction between Fe^{III} and Phen in the presence of $FeCp_2$ which lead to the formation of $Fe(Phen)_3^{2+}$. The latter reaction,

$$2\,Fe^{III} + FeCp_2 + 9\,Phen \rightarrow 3\,Fe(Phen)_3^{2+} + 2\,Cp$$

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* In the ligand exchange reaction (1) we prefer to call the reaction centre Fe^{III} rather than Fe^{I}. The total reaction must then be called a decomposition rather than a disproportionation reaction.

in particular, makes it impossible to use *o*-phenanthroline for the quantitative determination of Fe^{II} complexes in our solutions.

When I^- anions are added to a solution of $FeCp_2^+$ cations a different reaction occurs, namely reduction of $FeCp_2^+$ to $FeCp_2$:

$$2\,FeCp_2^+ + 2\,I^- \rightleftarrows 2\,FeCp_2 + I_2 \tag{4a}$$

At first sight this reaction looks a little puzzling, since it is known that $FeCp_2^+$ is formed when iodine is added to ferrocene[3] (*cf.* experimental section). It thus appears that reaction (4a) is in conflict with this observation. However, when ferrocene is oxidized by iodine never I^- anions are formed, but always I_3^- anions; so the oxidation of $FeCp_2$ by I_2 is not represented by the reverse of (4a), but by a combination of its reverse, (4b), with reaction (5):

$$2\,FeCp_2 + I_2 \rightleftarrows 2\,FeCp_2^+ + 2\,I^- \tag{4b}$$

$$\underline{2\,I^- + 2\,I_2 \rightleftarrows 2\,I_3^-} \tag{5}$$

$$2\,FeCp_2 + 3\,I_2 \rightleftarrows 2\,FeCp_2^+ + 2\,I_3^- \tag{6}$$

Now, although our results prove that the equilibrium (4b) lies to the left, the equilibrium for overall reaction (6) may still lie to the right, provided that equilibrium (5) lies far enough to the right. Unfortunately, the equilibrium constants of these reactions have not been determined in acetone and acetonitrile. They have, however, been measured in 1,2-dichloroethane, methanol and sulfolane[19–21], and in them it is, indeed, found that $K_6 \gg 1$ and $K_{4b} \ll 1$ (and $K_{4a} \gg 1$). The results also show that the equilibrium constants are strongly solvent-dependent[21]. The fact that in a given solvent, iodide reduces the ferricenium cation whereas iodine oxidizes ferrocene, thus arises from a fortuitous combination of the solvation free enthalpies of $FeCp_2^+$, I_2, I^- and I_3^-.

The difference in behaviour between iodide ions and chloride and bromide anions is easily explained by looking at the two possible ways in which these anions may interact with $FeCp_2^+$. In the decomposition reaction only the primary, and possibly rate-determining, step is dependent on the attacking anion:

$$FeCp_2^+ + n\,X^- \rightleftarrows FeX_n^{(3-n)+} + 2\,Cp^- \qquad \leftarrow I^-\,Cl^- \rightarrow$$

Since I^- is a much weaker donor than Cl^- [17], this equilibrium will be shifted much more to the left for I^- than for Cl^-. On the other hand, the reduction equilibrium:

$$2\,FeCp_2^+ + 2\,X^- \rightleftarrows 2\,FeCp_2 + X_2 \qquad \leftarrow Cl^-\,I^- \rightarrow$$

is shifted to the left for Cl^- and to the right for I^-. Thus Cl^- ions decompose $FeCp_2^+$ cations, whereas I^- ions reduce them.

Similarly we can explain the results of Nesmeyanov *et al.*[3] and others[2,4], who found that, depending on the reaction conditions, different products are formed when oxidizing ferrocene with halogens (compare Introduction). For, after the initial formation of X^- ions:

$$2\,FeCp_2 + X_2 \rightleftarrows 2\,FeCp_2^+ + 2\,X^-$$

association to X_3^- ions may take place:

$$X_2 + X^- \rightleftarrows X_3^-$$

The position of this association equilibrium determines which reaction products are formed. If the equilibrium position is to the right, as is the case for iodine in most solvents and also for chlorine and bromine at low temperatures, then the halide ions are transformed into trihalide ions. Consequently no halide ions are available for decomposition of $FeCp_2^+$ ions and $FeCp_2^+ \cdot X_3^-$ is the reaction product. At room temperature the Cl_3^- and Br_3^- ions are unstable, and half of the $FeCp_2^+$ is decomposed by halide ions:

$$FeCp_2^+ + 4\,X^- \rightarrow FeX_4^- + 2\,Cp^-$$

$$2\,Cp^- + X_2 \rightarrow 2\,Cp + 2\,X^-$$

so that ultimately $FeCp_2^+ \cdot FeX_4^-$ is formed.

This study has demonstrated that the $FeCp_2^+$ cation is unstable to decomposition by many, even quite weak, donor solvents and ligands. The reason for this is not that the Cp^- anion is such a weak donor, but that the coupling of the ligand exchange reaction to a set of reduction reactions and to an irreversible transformation of cyclopentadienyl radicals shifts the equilibrium position for the overall reaction to the right. That the Cp^- ion is indeed a strong donor to Fe^{III} is demonstrated by crystallographic studies[8,9], which show that the bonding between the iron ion and the Cp^- ions is not much weakened by oxidation of ferrocene.

EXPERIMENTAL

Reagents and solvents

Ferricenium triiodide was prepared by a method published by Nesmeyanov *et al.*[3], by adding a solution of ferrocene in carbon tetrachloride to a solution of iodine in carbon tetrachloride at 50° ($FeCp_2/I_2 = 1/5$). The polyiodide precipitate was recrystallized three times from acetone. Ferricenium picrate[22] and tetrachloroferrate[23] were made by published methods. Ferricenium tetrafluoroborate was made by oxidation of ferrocene with benzoquinone in benzene, followed by reaction with BF_3.

No special precautions were taken with respect to the solvents used, except that they were dried over molecular sieves. Analytical-reagent-grade tetra-n-alkylammonium halides, nitrate, perchlorate, and tetrafluoroborate were used without further purification.

Electron spin resonance measurements

ESR spectra of solutions contained in sealed quartz tubes were obtained with a Varian X-band V 4500 spectrometer, using 100 kHz field modulation. Measurements were performed with liquid solutions at room temperature (295°K) and with solid solutions at 77° and 20°K by placing the quartz tubes in a Varian ESR fingertip Dewar filled with liquid nitrogen and liquid hydrogen, respectively.

Susceptibility measurements

The susceptibilities of acetone and acetonitrile solutions were measured by an NMR technique[24] on a Varian A 60 NMR spectrometer. TMS was used both as an internal and external reference. We checked that there was no contact shift for TMS. In the solutions of $FeCp_2^+$ in acetone and acetonitrile we found, in addition to the paramagnetic bulk shift, a contact shift for the solvent proton lines. This points to interaction between the ferricenium cation and the solvent molecules and agrees with conclusions drawn from ESR experiments[7]. No contact shift was observed for the solvent proton lines in solutions of $FeCl_4^-$ salts in acetone or acetonitrile.

Spectrophotometric measurements

Visible and UV absorption spectra were taken on a Cary 14 recording spectrophotometer using quartz cells of 1.0 cm, with the solvent as a reference. Absorption measurements were carried out exclusively with $FeCp_2^+ \cdot BF_4^-$ in acetonitrile, since the BF_4^- anion and acetonitrile have no absorption bands in the visible and near-UV region, in contrast to other anions and solvents.

All experiments were performed with ferricenium picrate, triiodide and tetrafluoroborate. No differences in behaviour between these salts were found. In the decomposition reactions with halide anions, acetone, nitromethane and acetonitrile were used as solvents. In all three solvents the same results were obtained.

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