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# A Correlation Between the Photochemical Reactivity of the Metallocenes and Their Ions, and Their Electronic Structures

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*Quantum yields of decomposition have been measured for the photolysis of ferrocene, ruthenocene, nickelocene, cobaltocene, bisbenzenechromium and their respective cations. It was found that while the "18 electron" compounds were photostable, the others, all containing unpaired electrons were not. The results are discussed in terms of the electronic structures of the compounds. The ultra-violet spectra of nickelocenium chloride and cobaltocene were recorded.*

## Introduction

The object of the work was to study systematically the photolysis of metallocenes ($MCp_2$ where M is the metal ion and Cp is the cyclopentadienyl radical), to see if there is any correlation between photochemical reactivity and electronic structure in these molecules. Previous work[1, 2] has concentrated on the organic derivatives of metallocenes[3, 4, 5, 6], together with studies of the quenching behaviour of ferrocene[7] and of its effectiveness as a photosensitising reagent[8, 9, 10]. Ferrocene itself is remarkably photostable in hydrocarbon solvents[1, 11] although it reacts in halocarbons via a charge-transfer complex[12, 13, 14] to yield the ferrocenium cation $(FeCp_2)^+$. *Cis/Trans* photo isomerisation has been observed with *cis* styryl ferrocene[15]; unlike its analogue benzophenone, benzoyl ferrocene does not have clean photochemical reactions, but decomposes to uncharacterisable products[16, 17].

In our work we have measured quantum yields of decomposition for several compounds in hydrocarbon and aqueous solutions. The compounds without an "18 electron" structure all decompose but in every case the photolysis gave polymeric products.

## Experimental

Most of the reactions were carried out with a medium pressure mercury arc, using interference filters to isolate the appropriate spectral region. The reagents were contained in our small scale apparatus[18], and also in a modified square (1 cm) spectrophotometer cell, which was stirred and deaerated continuously with a stream of pure nitrogen[18]. The reactions were usually followed by spectrophotometry.

Ferrocene was obtained from B.D.H. chemicals, nickelocene and cobaltocene from Alfa inorganic chemicals and ruthenocene from Strem chemicals. The nickelocene was supplied in *o*-xylene, which was removed under nitrogen with a rotary evaporator. Diethylbenzene was similarly removed from the commercial cobaltocene mixture. The compounds were then further purified by vacuum sublimation.

The metallocene cations were prepared by stirring the metallocenes with constant boiling point HCl[19]. Ferrocene required several days for oxidation, but nickelocene and cobaltocene could be oxidised in a few hours. The solvents used were spectrograde; they were dried with $CaSO_4$ and then with $CaH_2$ or sodium wire.

## Results

Although the compounds are well characterised, the spectrum of $(Cp_2Ni)^+Cl^-$ has not been recorded, presumably because of its instability. Approximate values of the absorptivities of $(Cp_2Ni)^+Cl^-$ were obtained by taking spectra at known times after adding nickelocene to HCl to produce the cation. A known weight of nickelocene was stirred in 20 cm$^3$ of 2.76*M* HCl for a set time before 20 ml of cyclohexane was added. After vigorous shaking the mixture was separated and the amount of unreacted nickelocene was determined. Spectra were taken of the aqueous phase at successive times to determine the decrease in the absorption of the $(Cp_2Ni)^+Cl^-$ as it decomposed. By extrapolating the graphs back to zero time, and to the time of addition of the cyclohexane, maximum and minimum values could be estimated for the absorptivities. However, better values could be obtained by taking a reasonable rate model for the formation and decomposition, and solving for the rate constants and concentrations. The values recorded in Fig. 1 were obtained in this way. The error bars at 370 nm represent the maximum and minimum values determined by extrapolation.

Fig. 2 gives an approximate spectrum for cobaltocene. This was obtained by simply dissolving the solid material in cyclohexane. Since cobaltocene is also unstable, the values of the absorptivity given are only approximate.

Ferrocenium chloride was photolysed at its strong absorption band at 254 nm in both aqueous and aqueous methanolic solutions at concentrations between 3 and $6 \times 10^{-4} M$. In aqueous solution the only photoproduct was ferrocene itself, and the reaction was followed by observing the change in absorption at 283 nm, using the absorptivities of Harju and Peterson[20]. In aqueous HCl at acid concentrations of $0 \cdot 011 M$, $0 \cdot 276 M$ and $2 \cdot 76 M$, the quantum yield for the reaction was found to be $0 \cdot 029 \pm 0 \cdot 002$.

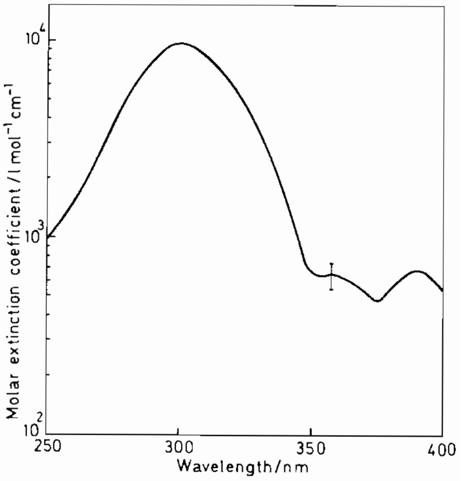

Figure 1. Absorption spectrum of Nickelocenium Chloride between 250 and 450 nm.

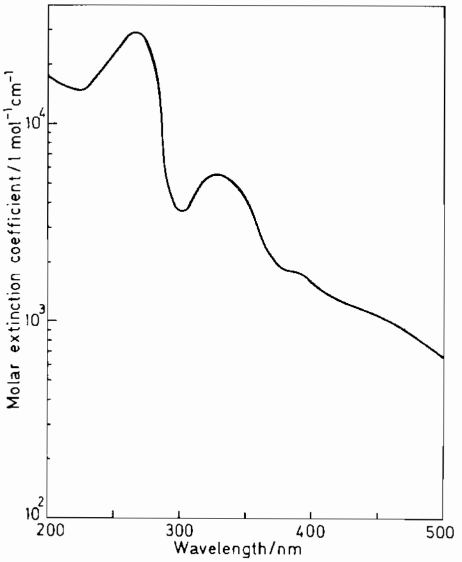

Figure 2. Absorption spectrum of Cobaltocene between 200 and 500 nm.

In aqueous acidic methanol, photoreduction was also observed, but decomposition occurred in dilute acid solution. The acidic methanol solutions were made up by diluting constant boiling point HCl ($5 \cdot 53 M$) with methanol, and the concentrations quoted are those of the acid in the total volume. Above $1 M$ acid only photoreduction occurs with virtually the same value as in aqueous solution; $0 \cdot 031 \pm 0 \cdot 002$. With dilute acid and more methanol, decomposition occurred and the spectrum of methoxylated ferric ions[21,22] were observed $[\mathrm{Fe(OMe)}]^{2+}$. The formation of these ions was monitored at 361 nm, and the quantum yield estimated after making a correction for the noticeable dark reaction. The quantum yield increased from $0 \cdot 13$ in $1 M$HCl to $0 \cdot 16$ in $0 \cdot 55 M$HCl and then remained at $0 \cdot 16$ for dilute acid solutions ($0 \cdot 22 M$, $0 \cdot 11 M$ and $0 \cdot 055 M$).

An attempt was made to identify the possible volatile photo-products from the cyclopentadienyl radical, but none was found. At long photolysis times photoreduction of the product ferric ions was observed[23].

Nickelocene was photolysed at 254 nm as a deaerated $0 \cdot 007 M$ solution in cyclohexane. A general decrease in absorption was observed, but no identifiable product was found other than a brown polymer after evaporation of the photolysed solution. The quantum yield of decomposition was estimated from the decrease in absorption at three wavelengths and was found to be $7 \cdot 0 \pm 0 \cdot 5 \times 10^{-3}$.

Nickelocenium chloride was photolysed immediately after the preparation as described above, in aqueous solution, at acidities of HCl between $0 \cdot 03 M$ and $2 \cdot 76 M$. After long photolysis times a yellow polymeric solid precipitated and $Ni^{2+}$ ions were observed in solution. The quantum yield of decomposition was estimated at short times by following the change in the spectrum (Fig. 1) and correcting for the appreciable dark reaction. It was found to be $0 \cdot 44 \pm 0 \cdot 02$.

Cobaltocene was photolysed at 254 nm in deaerated solutions in cyclohexane. Decomposition occurred but it was not possible to make an accurate estimate of the quantum yield as the dark reaction was rapid and the changes in optical density were not uniform with time. We can only say that photolysis accelerated the decomposition. The products which separate out from the solution are polymeric.

Bisbenzene Chromium Iodide was photolysed by Dr. J. Sedlar[24] of this laboratory, who estimated the quantum yield, from the quantity of benzene produced, to be $0 \cdot 18$ as previously found by Traverso and Scandola[12].

Ferrocene, Ruthenocene, Bisbenzene Chromium and Cobaltocenium Chloride were all irradiated at 254 nm in cyclohexane solution or, for the ion, in aqueous acidic methanol. Despite long irradiations no decomposition was observed and the quantum yields of decomposition were certainly less than $10^{-4}$ and probably zero.

## Discussion

The spectra of $(Cp_2Ni)^+Cl^-$ and $Cp_2Co$ are similar to those observed for the other metallocenes[25] with strong charge-transfer bands below ~320 nm, and medium strength *d–d* bands at longer wavelengths. Our values for cobaltocene do not agree well with the early measurements of Pfab and Fischer[26]; $Cp_2Co$ is unstable and it is possible that the earlier measurements were affected by this.

In Table I the results of the photodecomposition are given together with their probable electronic structures of the metallocenes based on the diagrams due to Dyatkina[25,27,28]. With the different reaction conditions used and the ignorance of the precise stoichiometry of the various reactions it is difficult to build too much upon the obvious correlations between photochemical reactivity and either the presence of unpaired electrons, or the presence of an electronic configuration other than those containing 18 electrons.

However, although most of the ions were photolysed in aqueous solution, and the parent compounds in hydrocarbon solution, the behaviour of the two cobalt compounds, where the reactivities and the solvent conditions are reversed, encourages us to believe that the correlation is real.

Similarly, the possibility that the photochemical activity is caused by charge-transfer complexes between cation and anion, similar to those between ferrocene or ruthenocene and halocarbons[12,13,14,29] can also be excluded with the cobaltocene example.

A possible explanation of the results is that the transitions activate the ring positions so that the molecule reacts with the solvent or another molecule. The transitions in the region of 254 nm have been assigned[25] to promotion of an electron from the $1e_{1u}$ orbitals to the $2e_{1g}$ orbital, that is from bonding orbitals between the rings and the metal with a predominantly ring-contribution, to antibonding orbitals to which the metal mainly contributes. These are thought to be the same for both the $d^5$ and the $d^6$ ions[25], and it is reasonable to assume that the $d^7$ and $d^8$ ions will be similar. The effect of the transition is to create a small extra positive charge on the ring positions, but as this is qualitatively the same for both the 18-electron and the other molecules, it is not possible to attribute activity to enhanced activation of the rings, without detailed calculations.

Another alternative is that the transition weakens the bonding in the molecule leading to metal/ring cleavage. With the stable $d^6$ configuration as a standard for the $MCp_2$ compounds, the extra electrons in the other ground state molecules are lost from either the $a_{1g}$ or $e_{2g}$ orbitals which are non-bonding or slightly bonding orbitals centred mainly on the metal, or gained by the $e_{1g}$ orbitals which are thought to be antibonding[25]. The results would then indicate that the bonding in these molecules is more finely balanced than would be estimated from a simple electron count; thus the transfer of a single electron from the $e_{2g}$ orbitals containing 4 electrons or the $e_{1g}$ which contains 1 or 2 electrons is enough to cause breakdown. For $(Cp_2Fe^+)$ the absence of an electron from one of the nearly non-bonding orbitals has a similar effect.

It is not possible to try to go further than this with the present results. It is evident that the answers to these problems may be yielded by flash photolysis studies, if the intermediates can be identified, rather than by steady state studies which are hampered by the formation of polymeric products.

TABLE I. The Photostability of Several Metallocenes.

| Compound | $\Phi$ | Number of Electrons | Configuration | Unpaired Spins |
|---|---|---|---|---|
| $Cp_2Fe^+$ | 0.16 | $d^5(17)$ | $(a_{1g}')^2\ (e_{2g})^3$ | 1 |
| $Cp_2Fe$ | 0 | $d^6(18)$ | $(a_{1g}')^2\ (e_{2g})^4$ | 0 |
| $Cp_2Ru$ | 0 | $d^6(18)$ | $(a_{1g}')^2\ (e_{2g})^4$ | 0 |
| $Cp_2Co^+$ | 0 | $d^6(18)$ | $(a_{1g}')^2\ (e_{2g})^4$ | 0 |
| $Cp_2Co$ | decomposes | $d^7(19)$ | $(a_{1g}')^2\ (c_{2g})^4\ (a_{1g}'')^1$ | 1 |
| $Cp_2Ni^+$ | 0.45 | $d^7(19)$ | $(a_{1g}')^2\ (e_{2g})^4\ (e_{1g})^1$ | 1 |
| $Cp_2Ni$ | 0.007 | $d^8(20)$ | $(a_{1g}')^2\ (e_{2g})^4\ (e_{1g})^2$ | 2 |
| $Bz_2Cr^+$ | 0.18 | $d^3(17)$ | $(e_{2g})^4\ (a_{1g})^1$ | 1 |
| $Bz_2Cr$ | 0 | $d^4(18)$ | $(e_{2g})^4\ (a_{1g})^2$ | 0 |

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