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The Photochemistry of Metallocenes

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The problems of the photochemistry of the dicyclopentadienyl derivatives of Group VIII metals are considered. Examples of the use of the photochemical reactions of metallocenes for the preparation of light-sensitive materials, inhibitors of the photoageing of polymers, catalysts of the photodecomposition of polymers, etc are presented.
The bibliography includes 125 references.

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I. INTRODUCTION

The photochemistry of metallocenes (dicyclopentadienylmetals) has been developing vigorously mainly during recent years. The planned investigation of the photochemistry of ferrocene and its derivatives as well as ruthenocene and osmocene was begun about 10 years ago in a number of countries. Data obtained up to 1977 are surveyed in a monograph[1] published in 1979; later reviews devoted to the photochemistry of metallocenes are not available in the literature. The aim of the present review is to survey the literature data on the photochemistry of metallocenes published mainly during the last 10–12 years. Attention has been concentrated on the photochemistry of the cyclopentadienyl derivatives of Group VIII metals, since these are most readily available and are of interest from the practical point of view.

II. FERROCENE AND ITS DERIVATIVES

We shall consider the current ideas about the electronic configuration of the ground and certain excited states of ferrocene and ferrocenium salts. The details of the electronic configuration are still the subject of discussion and the results of theoretical calculations are not always consistent with the experimental data obtained.[2-12]

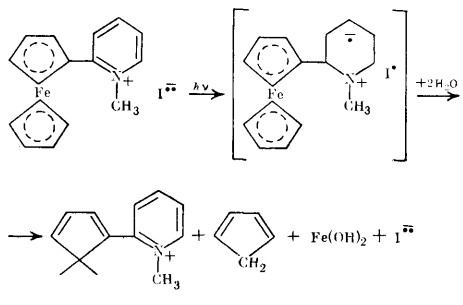
The distribution of the energy levels of ferrocene in the ground state has been investigated[13] on the basis of the EPR and photoelectron spectra (Fig. 1*a*). On photoexcitation, the ferrocene molecule passes from the $^1A_{1g}$ singlet state (or possibly from the $^1E_{2g}$ state) to the excited $^3E^*_{1g}$ triplet state (Fig. 1*b*). Oxidation results in the formation of the ferrocenium ion Fc^+ (doublet $^2A_{1g}$ state) (Fig. 1*c*). A similar estimate of the energies of the e_{1g} and a_{1g} levels of the ferrocenium ion constitutes the basis of the scheme presented in the monograph of Jeoffroy and Wrighton,[1] where these values are believed to be virtually identical.

The difficulties arising in the interpretation of the bands in the electronic spectra of ferrocene are indicated in another monograph.[14] For the interpretation of the bands in the electronic absorption spectra of ferrocene and other metallocenes, reliable experimental data are therefore required over the widest possible spectral range. To achieve reliability, studies by different and independent methods are essential.

The view that the ferrocene system is extremely resistant to various types of radiation existed for a long time in the literature.[15] For example, it has been stated that ferrocene is stable under irradiation[17] and also that the Szillard–Chalmers reaction has been carried out with ferrocene[16] in which irradiation of ferrocene with fast neutrons results in the formation of a metallocene containing ^{59}Fe; it is remarkable that this process proceeds without significant decomposition of the ferrocene system. The resistance of ferrocene to the action of light in solutions in decalin, cyclohexane, and alcohols has also been noted.[18]

However, subsequent studies showed that ferrocene and its derivatives are capable of undergoing photodecomposition reactions. The first studies on the photodecomposition of ferrocene derivatives containing electron-accepting substituents linked directly to the cyclopentadienyl ring[19,20] and also separated from it by vinyl[21] of phenylene[22,23] groups were carried out by Nesmeyanov, Sazonova, and coworkers. The decomposition of α-ferrocenyl-*N*-methylpyridinium salts has been studied in greatest detail[24-27] and the photodecomposition mechanism presented in Scheme 1 has been proposed for them.

Scheme 1



According to this mechanism, the transfer of an electron from the anion to the pyridinium system results in the formation of a relatively unstable intermediate species which decomposes under the influence of irradiation giving rise to 2-cyclopentadienyl-1-methylpyridinium, cyclopentadiene, and iron hydroxide.

Traverso and coworkers[28–33] investigated the processes occurring in the photolysis of ferrocene and its derivatives in different solvents. A detailed study of the photodecomposition of ferrocene in the presence of CCl_4 and $CHCl_3$ [28] showed that the process proceeds in a more complex manner than had been supposed by Brand and Sneddon.[29] It was found that the quantum yield of the photodecomposition is much greater than unity and depends appreciably on the ferrocene concentration in solution. The abstraction of an electron under the influence of radiation can be accompanied by a secondary chemical interaction of ferrocene with the reactive radicals $CCl_3^{\cdot}$ and $CHCl_2^{\cdot}$. Traverso and Scandola[28] observed bands in the absorption spectra of the reaction products which had been shown earlier by Nesmeyanov et al.[6] to correspond to charge transfer from the metal to the cyclopentadienyl ring. This constitutes an important confirmation of the proposed mechanism. If ferrocene is in an excited state, then the electron initially passes from the orbital associated mainly with the metal to one associated mainly with the ligand and is then abstracted. The absence of the products of the photochemical oxidation of ferrocene itself in the case of spectroscopically inactive solvents cannot serve as an argument in support of the mechanism involving charge transfer to the solvent molecule according to Traverso and Scandola,[28] because the abstraction of an electron in these solvents by radiation may become reversible.

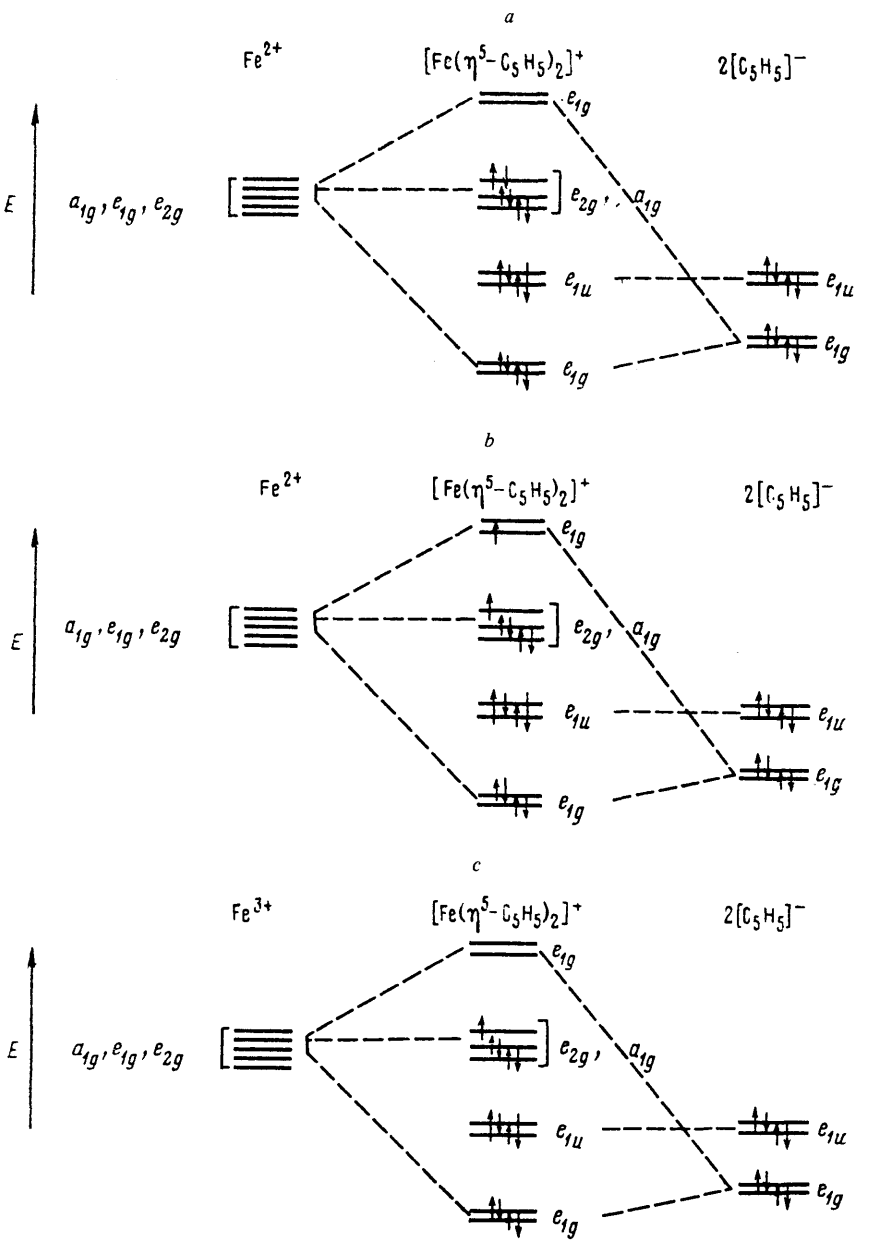


Figure. Energy level schemes for the ground (*a*) and excited (*b*) states of ferrocene (Fc^*) and the state of the ferrocenium ion (Fc^+) (*c*).

The photochemical behaviour of benzoylferrocene in solution in methanol, absolute ethanol, or 1-propanol under irradiation by monochromatic light in the range 313–472 nm has been investigated by Traverso et al.[30] Benzoylferrocene passes to an excited state and, after electron transfer, is oxidised to the corresponding benzoylferrocenium cation; the presence of a hydrogen bond between benzoylferrocene and the hydroxylated solvent facilitates this process. The authors[30] suggested that the substitution product is $RC_5H_4FeC_5H_5$, but were unable to identify it; it was isolated subsequently.[34–38]

The photolysis of ferrocene in alcohol in the presence of a mixture of halogenohydrocarbons has been studied.[34–38] The photolysis of ferrocene in ethanol in the presence of CCl_4 leads to the ethyl ester of ferrocenecarboxylic acid. When the photolysis is carried out in other alcohols, the reaction hardly occurs. Formylferrocene and ferrocenylmethanol are formed respectively in low yields in the presence of $CHCl_3$ and CH_2Cl_2.

In the photolysis of ferrocene in the presence of halogenohydrocarbons initially all this results in the formation of ferrocenium halide and the radical of the corresponding halogenohydrocarbon (Scheme 2*a*). The subsequent course of the reaction can be different. In the presence of an alcohol, ferrocene substitution products are formed and the reaction proceeds with formation of a new C – C bond; in the presence of acrylamide, either the latter polymerises or ferrocenium salts are formed (see Scheme 2, stages *e* and *f*).[37]

Scheme 2

$$[Fe(\eta^5\text{-}C_5H_5)_2] \xrightarrow[(a)]{h\nu,\ CCl_4} [Fe(\eta^5\text{-}C_5H_5)_2]Cl + \dot{C}Cl_3 \xrightarrow{(b)} [Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CCl_3)] + H^+ \rightarrow$$

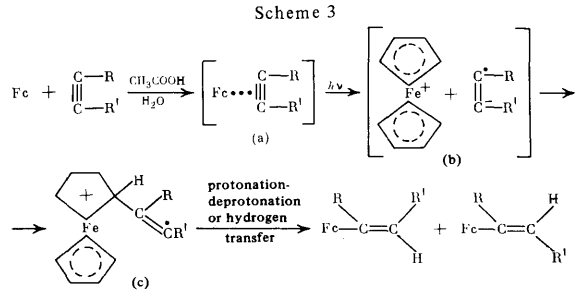
$$\rightarrow \left\{ \begin{array}{l} \xrightarrow[(c)]{C_2H_5OH} [Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4COC_2H_5)] \\ \xrightarrow[(d)]{} FeCl_3 \end{array} \right. ;$$

$$[Fe(\eta^5\text{-}C_5H_5)_2]Cl + FeCl_3 \xrightarrow{(e)} [Fe(\eta^5\text{-}C_5H_5)_2][FeCl_4] ;$$

$$\dot{C}Cl_3 + \text{acrylamide} \xrightarrow{(f)} \text{polyacrylamide}.$$

It has been established[38] that, when a mixture of ferrocene and dimethyl acetylenedicarboxylate is irradiated with ultraviolet light in an aqueous acetic acid solution, a mixture of dimethyl ferrocenylmaleate and dimethyl ferrocenylfumarate is formed. If acetylenedicarboxylic acid, methyl 3-carbamoylpropiolate, acetylenedicarboxylic acid dinitrile, or methyl propiolate are used instead of dimethyl acetylenedicarboxylate, the corresponding ferrocene derivatives are formed. It is noteworthy that acetylene derivatives containing electron-accepting substituents enter into the reaction in this case; it is believed[37,38] that the reaction mechanism involves the initial stage in which a charge-transfer complex is formed and then decomposes into the ferrocenium cation and a radical-anion (Scheme 3*b*); this is followed by the formation of the ferrocenium radical-cation (Scheme 3*c*), which is converted into methyl β-ferrocenylacrylate (for R = H) or into a mixture of derivatives of maleic and fumaric acids (for R = $COOCH_3$).[38]

Scheme 3



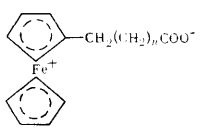
R = R' = CO_2CH_3; R = CO_2CH_3, R' = $CONH_2$; R = H, R' = CO_2CH_3; Fc = $C_5H_5FeC_5H_5$.

When acetone, acetonitrile, ethyl acetate, or methanol were used as solvents, the yield of substitution products was appreciably lower.

The use of nitrous oxide in the study of the photochemistry of ferrocene made it possible to follow the course of the electron transfer process and to estimate the quantum yield of the overall reaction from the amount of gaseous nitrogen evolved.[39–49] Apart from ferrocene,[39,40] the photochemistry of methyl-, 1,1'-dimethylphenyl-, and acetyl-ferrocenes[41,42] has been studied by this method. Electrochemical and photochemical data have demonstrated the similarity of the influence of the substituent on the abstraction of an electron from the ground and photoexcited states; the quantum yield was appreciably less than unity under these conditions.

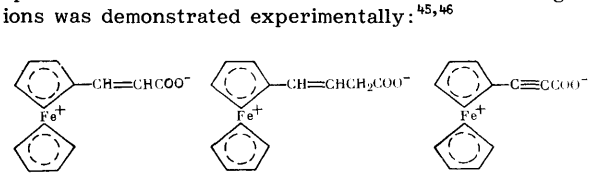
Nitrous oxide has also been used in the study of the photochemical behaviour of ferrocenylalkane- and ferrocenylalkenecarboxylic acids[42–46] on irradiation with light at a wavelength of 254 nm. It was shown that the quantum yields of the processes vary linearly with the N_2O concentration. The authors suggest that the low quantum yield can be accounted for by the fact that the photoinitiated stage is not the only one occurring on absorption of light and is accompanied also by a dark reaction. Thus direct electron transfer from the ferrocenyl component of the molecule to N_2O is believed by the authors to be more probable than electron transfer to the hydroxylated solvent. This is demonstrated by the presence in the irradiated specimens of cyclopentadiene, detected by means of gas–liquid chromatography.

Subsequently the same workers[45–47] showed that on photoirradiation the electron can readily pass from the excited triplet state of the ferrocene molecule to an acceptor of the type N_2O; the lifetime of the excited triplet state is then extremely short, amounting to 1 μs. In an alkaline medium the product of such transfer exists in the form of a stable dipolar ion:



It was found that the electronic absorption spectrum of such a dipolar ion resembles that of ferrocenium salts. Chemical reduction led to the recovery of the initial acid. Thus the process proceeds without the decomposition of the ferrocene system.

In the same series of investigations[41,42] studies were made not only of the reactions of β-ferrocenylpropionic acid in aqueous alkaline media (borate buffer at pH 9–10) but also chain growth was achieved and the resulting γ-ferrocenylbutyric and δ-ferrocenylvaleric acids were studied in order to check that intramolecular electron transfer occurs on photoexcitation.[44] However, a chain of four–five carbon atoms with free rotation about a single bond can at some instant occupy a position such that the carboxylate anion is fairly close to the iron atom. The authors therefore subsequently investigated the photolysis of ferrocenylalkene- and ferrocenylalkyne-carboxylic acids in the molecules of which the double or triple bond rules out the possibility of the rotation of the chain and the approach of the "COO" group to the iron atom. The existence of the following dipolar ions was demonstrated experimentally:[45,46]



The dipolar ions are formed as a result of the irradiation of the corresponding acids with light at a wavelength of 240 nm in an aqueous borate buffer in the presence of N_2O. The author suggests that three processes take place under these conditions:[46] (1) photoexcitation of the molecule in the ground state to a short-lived triplet state (a first-order reaction); (2) reaction with N_2O, giving rise to the dipolar ion and N_2; (3) quenching of the excitation induced by the addition of alcohols.

Thus in solvating solvents and also in the presence of electron acceptors, both in solution and incorporated in the molecule of the test substance, ferrocene and its derivatives undergo complex photolytic and oxidation processes, which in some instances are accompanied either by substitution in the cyclopentadienyl ring with formation of new C–C bonds or by the decomposition of the ferrocene system.

When ferrocene and its derivatives are exposed to visible light in alcohol in the presence of oxygen, no less complex processes occur. However, they are not accompanied by the decomposition of ferrocene, its homologues and ferrocenium salts. The auto-oscillatory photochemical processes occurring in alcoholic solutions of ferrocene, octamethylferrocene, and the corresponding ferrocenium hexafluorophosphates on irradiation with visible light from a 500 W incandescent lamp have been described for the first time in a number of communications.[50-54] A periodic increase and decrease of the intensity of the bands in the absorption spectra of solutions of this substance were observed under these conditions. It was established that the period of the oscillation of the intensity increases with increase of the concentration of the solution, decreases with increasing temperature, and depends on the concentration of oxygen in the system. There is an oxygen concentration at which the period of the oscillations is a minimum.[52] A mechanism has been proposed for this multistage process with participation of alcohol and oxygen, in which ferrocene plays the role of the photosensitiser.[54]

The reaction between alcohols and alkyl isocyanates, catalysed by the light-sensitive ferrocene–$FeCl_3$ system, has been examined by Wilfutte-Steinert.[55] The kinetics of the interaction of t-butyl isocyanate with methanol in the presence of ferrocene at 25 °C have been investigated by infrared and ultraviolet spectroscopy in solution in the CCl_4–CH_2Cl_2 mixture under illumination with monochromatic light at 365 nm. After an induction period of 15 min, the rate of decomposition of t-butyl isocyanate obeys a zero-order kinetic equation; this is associated with the absorption of light by the $FeCl_4^-$ ions which are formed on irradiation of ferrocene in CCl_4 and absorb 99% of the incident light after 30 min of reaction. An ionic-chain mechanism with radical initiation has been proposed for the reaction. The initiation stages

$$Fe^{3+} + Cl^- \xrightarrow{h\nu} Fe^{2+} + \dot{C}l$$
$$\dot{C}l + RNCO \rightarrow RNCO^+ + Cl^-,$$

are accompanied by chain propagation reactions:

$$RNCO^+ + R'OH \rightarrow \overset{+}{R}NHCOOR' \rightarrow RNHCOOR' + RNCO^+.$$

The quantum yield of the reaction is 0.3. Another possible mechanism has been proposed for the chain propagation stage:

$$RNCO^+ + Fe^{2+} \rightarrow RNCO + Fe^{3+}.$$

The consumption of Fe^{3+} is compensated by the oxidation of Fe^{2+} by the ferrocenium cation.

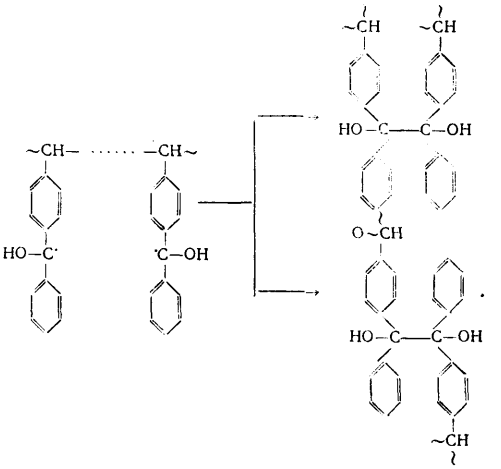
Certain ferrocene derivatives, for example, ketones, behave specifically under illumination. It is known that aromatic ketones are readily converted into pinacones on irradiation. However, this type of reaction has not been observed for ketones of the ferrocene series: on irradiation in the presence of proton or electron donors, they give rise to the corresponding ferrocene alcohols:

$$Fc{-}COR \xrightarrow{h\nu} Fc{-}\underset{\displaystyle OH}{\underset{|}{C}}HR,$$

where R = H, CH_3, or C_6H_5.[56] In propanol this reaction proceeds with an insignificant quantum yield (~0.002). It has been stated[18] that the photodecomposition of acetylferrocene is hardly observed in isopropyl alcohol. However, when the reaction is carried out in the presence of reductants [$(C_4H_9)_3SnH$ and $(C_6H_5)_3SnH$], the photochemical reduction of acetylferrocene leads to the corresponding alcohols with a quantum yield higher by an order of magnitude (~0.02).[56] The authors believe that in the excited state the oxygen atom of acetylferrocene can have a distinctly radical character and that photoexcitation is due to the $d \cdot d$ transitions at the central iron atom and not the $n \cdot \pi^*$ transitions in the ligand. Consequently the reduction of ketones derived from ferrocene is due to the low energy of the excited state.

Sandez et al.,[57] who investigated the chemical behaviour of vinyl-benzophenone (VBP) polymers and VBP–vinylferrocene copolymers on irradiation, adhere to similar ideas. It has been found that the morphology of the polymer chains in the VBP polymer changes significantly as a consequence of the photochemical oxidation and intramolecular processes (cyclic and cross-linked structures appear–see Scheme 4).

Scheme 4



The polymer then becomes brittle and acquires some undesirable properties. On the other hand, irradiation of VBP–vinylferrocene copolymers in the presence of isopropyl alcohol does not entail significant changes in their physicochemical properties. These data permit the conclusion that ferrocene derivatives inhibit the photoageing processes in polymers.

A new absorption band has been observed in the electronic absorption spectrum of a solution of ferrocene in CCl_4[58] and was assigned to charge transfer to the solvent. The irradiation of this solution results in the formation of ferrocenium tetrachloroferrate $[C_5H_5FeC_5H_5]^+FeCl_4^-$.

The photochemical reactions of charge-transfer complexes (CTC) based on ferrocene or its derivatives and polyhalogenohydrocarbons (CBr_4) have been studied in detail recently.[60-64] The investigation of the spectroscopic characteristics of the CTC formed on interaction of CBr_4 with ferrocene or its derivatives showed that the ferrocene molecule forms a complex with three CBr_4 molecules.[59] The introduction of substituents into the ferrocene molecule alters the composition of

the CTC produced. Monosubstituted ferrocene derivatives form a complex incorporating two CBr_4 molecules. The introduction of substituents into both cyclopentadienyl rings alters the composition of the complex to one corresponding to the 1 : 1 ratio.

Investigation of the influence of the substituent on the position of the absorption band maximum in the electronic spectra of monosubstituted and heteroannular disubstituted ferrocene derivatives with electron-donating and electron-accepting substituents showed[4,6,11] that the shift of the long-wavelength band maximum at 440–560 nm resulting from the introduction of substituents into ferrocene is not great (3–15 nm), but it depends appreciably on the electronic character of the substituent. The 440 nm band undergoes a small hypsochromic shift in the case of electron-donating substituents and a bathochromic shift in the case of electron-accepting substituents.[6]

On the other hand, when CTC are formed, the influence of the substituents on the spectrum is much greater: the band shift amounts to 50–100 nm. The introduction of electron-accepting substituents into the ferrocene molecule causes a hypsochromic shift of the CTC band maximum, while the introduction of electron-donating (alkyl) groups results in a bathochromic shift. The greatest displacement of the CTC band maximum is observed in the electronic spectrum of the symmetrical octamethylferrocene;[10] λ_{max} for the ferrocene–CBr_4 CTC differs from λ_{max} for octamethylferrocene–CBr_4 CTC by 112 nm. All these factors permit the selection, by varying the chemical nature of the substituent in one or both cyclopentadienyl rings of ferrocene, of systems whose photosensitivities lie within a wide range in the spectrum.

The formation of CTC by ferrocene and its derivatives with tetranitromethane in methanol has been demonstrated.[64,65] The authors of both studies postulate the formation of a ferrocene-tetranitromethane CTC in accordance with the scheme

$$C_5H_5FeC_5H_5 + C(NO_2)_4 \rightarrow C_5H_5FeC_5H_5 \cdot NO_2 + C(NO_2)_3^{\cdot}.$$

It has been shown[65] that ferrocene derivatives such as vinyl-, acetyl-, 1,1'-dimethyl-, 1,1'-diethyl-, and benzoyl-ferrocenes also form CTC with nitromethane.

The photochemical reaction between ferrocene and iodine in water has been studied by flash photolysis.[66,67] It has been established that the photodissociation of the iodine molecule (I_2) is followed by the two-stage formation of ferrocenium tri-iodide:

$$C_5H_5FeC_5H_5 + I \rightarrow C_5H_5FeC_5H_5^+ I^-,$$

$$C_5H_5FeC_5H_5^+ I^- \xrightarrow{I_2} C_5H_5FeC_5H_5^+ I_3^-,$$

which proceeds much more vigorously than the recombination of iodine atoms.

The photoinitiated interaction of ferrocene with iodine in benzene has been studied by flash photolysis[68] and it has been shown that the reaction proceeds as follows:

(1) the iodine molecule initially undergoes photodissociation into atoms and an iodine-benzene CTC is formed:

$$I + C_6H_6 \rightarrow C_6H_6 \cdot I;$$

(2) this is followed by the oxidation of ferrocene with atomic iodine (or the oxidation of the iodine–benzene CTC) with formation of the ferrocenium iodide ion pair:

$$I \cdot C_6H_6 \rightarrow C_5H_5FeC_5H_5^+ I^- + C_6H_6;$$

(3) finally ferrocenium iodide reacts with another iodine molecule to form ferrocenium tri-iodide:

$$C_5H_5FeC_5H_5^+ I^- + I_2 \rightarrow C_5H_5FeC_5H_5^+ I_3^-.$$

It has been established that the last two processes have similar rates.

1. Ferrocenium Salts

Hitherto the photodecomposition of ferrocenium salts has not been studied in detail. It has been reported[58] that the photolysis of ferrocenium tetrachloroferrate in a $CCl_4 + C_2H_5OH$ mixture results in the formation of only ferrocene and a small amount of hexachloroethane owing to the recombination of the trichloromethyl radicals produced on irradiation.

The photolysis of ferrocenium chloride has been investigated[69] in aqueous acid $H_2O|CH_3OH|HCl$ media and the formation of ferrocene with a quantum yield of 0.029 was observed. In more dilute acid solutions, decomposition to inorganic iron (II) salts takes place

III. RUTHENOCENE AND OSMOCENE

In contrast to ferrocene, an emission spectrum has been observed for ruthenocene which is fairly well resolved at a low temperature. The presence in this spectrum of the $d \cdot d$ transition band at 510 nm and the ability of ruthenocene to quench excited triplet states are attributed to the presence of a triplet level in the energy spectrum of its excited molecule.[2]

Independent studies by two groups of workers[2,70] showed that the photochemical behaviour of ruthenocene has much in common with that of ferrocene. On irradiation with light at a wavelength of 254 nm in cyclohexane, ruthenocene is inert, while in the presence of halogenohydrocarbons photolysis takes place, as for ferrocene, with the appearance of a charge-transfer band and oxidation to the ruthenocenium cation.

Thus, analogously to the photolysis of ferrocene, the process proceeds in accordance with the scheme

$$C_5H_5RuC_5H_5 + RCl \xrightarrow{h\nu} [C_5H_5RuC_5H_5]^+ Cl^- + R^{\cdot}.$$

Further irradiation leads to the appearance of turbidity in the solution and the precipitation of ruthenocenium tetrachlororuthenate. When the photolysis is carried out in the presence of acrylamide, the latter polymerises, which indicates indirectly the presence of radicals in the system. The quantum yield is high and, according to the data of different workers, assumes values ranging from 0.6 to 1. It may be that part of the ruthenocene is oxidised by a secondary reaction to ruthenocenium tetrachlororuthenate.

In later investigations, Traverso and coworkers[43] studied the photolysis of ruthenocene, benzoylruthenocene, and osmocene in the presence of tetracyanoethylene (TCE). The formation of complexes between the metallocene and TCE was then established by ultraviolet spectroscopy. Charge-transfer bands were observed at the boundary between the visible and infrared regions (720–830 nm). The authors discovered a linear relation between the position of the charge-transfer band maximum for the metallocene–TCE complexes in the electronic absorption spectrum in cyclohexane and the oxidation potential $E_{1/4}$; on this basis, they concluded that the TCE molecule is coordinated to the metal atom. In this connection the authors suggest that the difference between the energies of the two maxima on the absorption curve of the charge-transfer bands is associated with the difference between the energies of the two highest occupied orbitals of the metal. The difference between the energies of the $a_{1g}(d)$ and $e_{2g}(d)$ orbitals is 1452 cm^{-1} and corresponds to the difference between the ionisation energies obtained for the He-photoelectron spectra of ruthenocene and osmocene.[71] This result also constitutes an argument in support of the direct involvement of the metal atom in the bond with TCE, i.e. it is probable that the electron pair participating in the formation of the CTC is localised mainly at the metal.

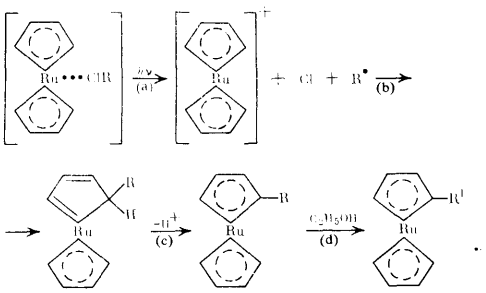
The photolysis of the CTC involves the following processes:

$$C_5H_5MC_5H_5 \cdot TCE \xrightarrow{h\nu} [C_5H_5MC_5H_5 \cdot TCE]^* \rightarrow \begin{cases} \longrightarrow C_5H_5MC_5H_5 + TCE \\ \longrightarrow [C_5H_5MC_5H_5]^+ + TCE^-; \end{cases}$$

M=Ru, Os .

The quantum yield in the formation of TCE is 0.75–0.68 and is independent of the wavelength of the incident light.

Sujimori et al.[72] carried out the photochemical ethoxymethylation, formylation, and ethoxycarbonylation of ruthenocene on irradiation of the latter in alcohol in the presence of the corresponding halogenohydrocarbons; the yields amounted to 10–20%. In the case of $CHCl_3$, formylruthenocene is formed in 39–57% yield on irradiation from a light source fitted with a pyrex glass filter. The authors presented the following process mechanism:



The reaction proceeds analogously to that described above for ferrocene.

Thus the photochemistry of ruthenocene has much in common with that of ferrocene; the reactions of both metallocenes take place via two pathways: (1) the oxidation of the metallocene and (2) further reactions with formation of new C–C bonds.

IV. COBALTOCENE AND NICKELOCENE

When cobaltocene is irradiated with light at a wavelength of 254 nm, it is oxidised and the cobaltocenium cation, stable under the irradiation conditions, is formed readily.[73] This is confirmed by the possibility of the quantitative spectrophotometric determination[73] of the cobaltocenium cation in aqueous solution over a wide pH range.

Aqueous solutions of cobaltocenium salts exhibit not only light stability but also radiation stability.[74,75] It is noteworthy that the character of the ultraviolet spectra of the cobaltocenium cation remains unchanged also after prolonged heating of its aqueous solutions at 200 °C.[75] Thus the photochemical behaviour of cobaltocene differs appreciably from that of the other metallocenes.

In contrast to cobaltocene, when nickelocene is irradiated with light at a wavelength of 254 nm, a polymer is formed and the quantum yield is 0.007. The primary oxidation product (nickelocenium chloride) rapidly decomposes to Ni^{2+} and a yellow deposit of the polymer,[76] i.e. nickelocene is extremely unstable in relation to ultraviolet irradiation.

V. PRACTICAL APPLICATIONS OF METALLOCENES IN PHOTOCHEMICAL PROCESSES

Patent data on the use of ferrocene as the main component of a light-sensitive composition were published in 1965.[77–79] Apart from ferrocene, CBr_4 and tone-controlling compounds were introduced into the light-sensitive composition. On exposure to light from an incandescent lamp and subsequent thermofixation, brown-violet images were obtained.

Highly sensitive materials have been developed on the basis of ferrocene, CBr_4 and a polymeric binder.[80] Subsequent studies designed to improve the compositions based on a number of ferrocene derivatives led to the creation of a whole series of light-sensitive materials. Light-sensitive emulsions containing ferrocene derivatives, a halogenohydrocarbon, and indole have been developed. The ferrocene derivatives employed were 1,1′-diacetylferrocene, 1,1′-dipropionylferrocene, 1,1′-dibenzoylferrocene, 4-(dimethylamino)-benzoylferrocene, and ferrocenedicarboxylic acid. A characteristic feature of these emulsions is their photosensitivity in the visible region of the spectrum.[81,82] It has been established that, by introducing aromatic aldehydes[83,84] into these photosensitive emulsions, it is possible to obtain multi-coloured images. In this connection it has been stated that in the presence of aldehydes[85] a deepening of the colour of the resulting image is achieved and the image becomes more distinct; the causes of this phenomenon are not discussed in the relevant patent.

Copying materials for microfilming,[86] containing polyvinylcarbazole, ferrocene, halogenohydrocarbons, and aromatic aldehydes have been described. Light-sensitive compositions based on imidazole derivatives, halogeno-derivatives, and ferrocene have been developed in the Federal Republic of Germany.[87]

Later, as the chemistry of ferrocene developed, more complex ferrocene-containing compounds began to be introduced into light-sensitive compositions.[88] A photographic material in which an emulsion containing ferrocene derivatives having the general formula

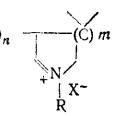
$$X{-}C_5H_4FeC_5H_4{-}Y$$

$$X{=}CO(CH{=}CH)_n\,Ar;\ n = 1, 2;\ Y{=}H, X$$

was deposited on baryta paper has been described.[89,90] An alcoholic solution of the test substance was deposited onto baryta paper and the latter was dried. The exposure was under an incandescent 500 W lamp for 5–11 min. In order to remove the unexposed sections, the emulsions were treated with solvents, which consisted of methanol or ethanol. The images obtained were predominantly of a yellowish-red colour.

It is noteworthy that water-soluble materials have also been developed on the basis of ferrocene in which the light-sensitive components were ferrocene-containing dyes[91] of the type

$$C_5H_5FeC_5H_4{-}(CH{=}CH)_{n+1}\,R' \quad \text{or} \quad C_5H_3FeC_5H_4{-}(CH{=}CH)_n$$



R = alkyl; R′ = pyrylium salt;

X=Cl′, Br, I; $n = 1$–3; $m = 1, 2$.

When vinyl groups are introduced, a long conjugated system is created and the absorption maximum of these compounds undergoes a bathocromic shift. The dyes synthesised were used to obtain light-sensitive materials which suffered from the disadvantage of a comparatively low light-sensitivity: in order to obtain a visible image, the emulsions had to be exposed for 4–6 min under a 2000 W lamp and then heated to 150 °C.

Charge-transfer complexes based on ferrocene, vinylferrocene, and various electron acceptors, which possess light-sensitive properties, have been recommended as optical filters absorbing in the range 350–600 nm.[92]

A negative light-sensitive material, sensitive both in the ultra-violet and in the visible part of the spectrum, has been prepared from ferrocene, halogeno-derivatives, and tone-controlling compounds with addition of polystyrene dissolved in trichloroethane.[93]

A light-sensitive composition for lithographic plates[94] has been obtained from a polymer with unsaturated ethylene groups or groups containing two or three chlorine or bromine atoms linked to one carbon atom and ferrocene derivatives (for example, thioacetylferrocene and 1,1'-dicinnamoylferrocene).

There have been a number of studies devoted to the mechanism of the intensification of the latent image in light-sensitive emulsions based on ferrocene.[95-97]

In 1971 a copying material containing the ammonium salt of ferrocenemonosulphonic acid or ferrocenedisulphonic acid or their mixture as well as a phenol residue containing the amino-, hydroxy-, or carbonyl groups in the *ortho*-position was developed in Japan in 1971.[98] A composition based on an organohalogen compound and a copolymer containing vinylferrocene and hardening on exposure to light has been patented.[99] Similar copolymers based on vinylferrocene are used in various photographic materials.[100] A patent[101] describes a positive material, sensitive to electrons and X-rays and other types of radiation, containing a copolymer of 1–30 mole % of vinylferrocene and 70–99 mole % of methacrylic acid.

A composition containing an organic halogen compound, aniline dyes, and ferrocene has been recommended for the formation of a coloured image.[102] A light-sensitive material for the formation of a black and white image by the dry method and based on ferrocene, organic dyes, and a halogeno-derivative giving rise to free radicals under the influence of light has been described.[103]

It is noteworthy that the entire patent literature contains as a rule only qualitative descriptions of light-sensitive compositions and emulsions based on them. In the literature there are virtually no physicochemical data and sensitometric and other characteristics of the materials obtained; it is therefore impossible to carry out an objective assessment of the light-sensitive characteristics of the proposed compositions or reach any conclusions about the likely usefulness of a particular composition from the standpoint of its practical applications.

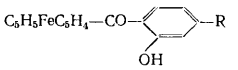
Metallocene derivatives are also used as photoconductors in electrophotography. Ferrocene, cobaltocene, and nickelocene have found the most extensive applications for these purposes.[104,105] Styrenebutadiene raw rubbers are used as binders and pyrylium salts are added as sensitisers.

The product of the condensation of formylferrocene with added organic halogeno-derivatives has been proposed for the preparation of polymeric ferrocene-containing emulsions for electrophotography.[106,107] A high-quality electrophotographic material has been obtained on the basis of polyvinylferrocene.[108] It permitted the repeated recording of an image.

When aromatic amino-derivatives, dyes, halogenohydrocarbons, and organometallic compounds[109] (ferrocene and cobaltocene) are added to a photoconductor based on polyvinylcarbazole or its brominated analogue, the photoconduction process is accelerated.[110] Thus a photoconductor containing cobaltocene can be exposed at 80 lux, while in the absence of added cobaltocene the exposure is 280 lux. It has been suggested that nickelocene be also used for these purposes.[111] A photoconducting composition suitable for the preparation of copying photoconductive emulsions based on polymeric compounds derived from formylferrocene has been obtained.[112]

It has been reported that metallocenes behave as photoinitiators in polymerisation.[113,114]

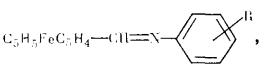
It is known that many ferrocene derivatives are capable of photostabilising various polymers.[115,116] For example, derivatives of hydroxybenzoylferrocene are used to stabilise polyolefins:[117]



R=OH, NO_2, C_2H_5, C_6H_5, $COCH_3$, COOH

Oxygen-containing,[118-120], silicon-containing,[121] and other derivatives of ferrocene[122] have been proposed as light stabilisers for polymers.

In order to improve the resistance of polyethylene to ultraviolet radiation, the oxime of acetylferrocene[123] or ferrocene-containing azomethines,[124] having the general formula



R = H, OH,

are introduced into the polymer.

The influence of ferrocene added to high-pressure polyethylene on the photodegradation of the polyethylene film has been investigated. It has been suggested that ferrocene and its derivatives catalyse the radical decomposition of the hydroperoxy-groups in polyethylene. The addition of ferrocene and its derivatives can be used to obtain materials which rapidly decompose under natural conditions.[125]

As can be seen from the foregoing, the photochemical processes involving metallocenes proceed as a rule via two pathways: either with the consumption of the metallocenes or with retention of the metallocene system and the formation of the product of substitution in the cyclopentadienyl ring. The photolysis of ferrocenium salts results in the formation of mainly ferrocene.

The photochemistry of ruthenocene has much in common with that of ferrocene. Analysis of the literature data on the photochemistry of metallocenes permits the conclusion that metallocenes containing an even total number of valence electrons are more stable, whereas those with an odd number of valence electrons are less stable.

Studies of the photochemical transformations in metallocenes are of great interest, since they make it possible to develop on the basis of these compounds materials which are finding practical applications in various systems for the recording, treatment, and replication of information.

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