Journal of Organometallic Chemistry, 365 (1989) 341–346
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 09624

Radical-forming electron-transfer; photoreactions involving iron group metallocenes

Paola Bergamini, Silvana Di Martino, Andrea Maldotti, Silvana Sostero, and Orazio Traverso

Dipartimento di Chimica - Centro Fotoreattività e Catalisi del C.N.R., Università di Ferrara, Via Borsari 46, 44100 Ferrara (Italy)

(Received October 5th, 1988)

Abstract

Iron group metallocenes Cp_2M ($Cp = C_5H_5$, M = Fe, Ru, Os) and chlorocarbon solvents RCl (CCl_4, $CHCl_3$, CH_2Cl_2, C_2Cl_4) form electron donor-acceptor (EDA) complexes. During irradiation of EDA complexes in the presence of spin traps, nitroxide radical adducts of chlorocarbon radicals $^{\cdot}R$ have been detected, and on this basis a mechanism for the photolysis of EDA complexes is suggested. The ability of metallocenes, particularly Cp_2Fe, to trap transient radicals $^{\cdot}R$ in electron transfer processes has been demonstrated.

Introduction

Electron donor-acceptor or EDA complexes are commonly encountered as intermediates in a wide variety of reactions involving as donors (D) electron-rich species such as nucleophiles and bases, and electron-deficient acceptors (A) [1]. For example metallocenes form EDA complexes with the percyanocarbon acceptors fumaronitrile, tetracyanoethylene, etc. [2]. One type of EDA complex of particular note is that between an iron group metallocene and a halocarbon solvent, involving a charge-transfer-to-solvent (CTTS) intermolecular process [3,4]. Previous investigations [3,4] of a series of metallocenes in halocarbon solvents established that selective irradiation within the CTTS absorption band leads directly to a single electron transfer process, i.e.:

$$Cp_2M + RCl \rightleftarrows \underset{\text{EDA complex}}{\{Cp_2M \cdot RCl\}} \xrightarrow[\text{CTTS}]{h\nu} Cp_2MCl + {}^{\cdot}R \qquad (1)$$

$(Cp = C_5H_5;\ RCl = CCl_4, CHCl_3, CH_2Cl_2)$

Observation of such a processes is consistent with the predictions of the Mulliken theory [5,6] that CTTS excitation results in the promotion of an electron from the highest occupied molecular orbital (HOMO) of the donor to the lowest unoccupied molecular orbital (LUMO) of the acceptor. The radicals $^{\cdot}R$ escape into the solution, where they may combine bimolecularly or form derivative of metals, leaving behind the species product Cp_2MCl.

The interest in the CTTS chemistry of iron group metallocenes in halocarbon solvents is two-fold. Since paramagnetic species are easily detected by spectroscopy, their presence can be taken as evidence for photoinduced electron transfer reaction. Moreover the detection and study of the reactions of radicals $^{\cdot}R$ (especially $^{\cdot}CCl_3$) is important in itself in view of the recognition that $^{\cdot}CCl_3$ radicals are a key intermediate in the metabolism and hepatoxicity of CCl_4 responsible for liver cell injury [7].

Experimental

Materials

All solvents used for spectroscopy and photochemistry are commercially available in spectroscopic grade.

The Cp_2M ($M = Fe,Ru,Os$, $Cp = C_5H_5$) were prepared by standard methods and their identities confirmed their IR and NMR spectra. Spin traps, *N*-t-Butyl-phenylnitrone (PBN) and nitrosobenzene (ArNO) were high purity materials from Aldrich.

Spectra

All UV-VIS spectra were obtained with a Perkin–Elmer recording spectrophotometer. Accurate difference spectra were obtained by the following illustrative procedure. Solutions of Cp_2M in 75% chlorocarbon–25% CH_3OH were made up by halocarbon dilution of 1 ml aliquots of a stock CH_3OH solution containing 10^{-2} *M* Cp_2M. A reference solution was made by similarly diluting the stock solution with CH_3OH. By using matched 10 cm path length quartz cells and scanning slowly to allow for slit with equilibration, the difference spectra were recorded with the halocarbon solution in the sample beam and the CH_3OH solution in the difference beam.

Photolyses

In a typical experiment, 3.0 ml samples of a solution containing $2 \cdot 10^{-3}$ *M* of Cp_2M were placed in quartz cuvette and degassed with N_2. Photolyses were performed with a Bruker medium-pressure lamp. With corning glass filters to isolate 313 and 366 Hg emissions or with a 250 W xenon lamp equipped with f/3.4 Applied Photophysics monochromator. Actinometry was accomplished with ferrioxolate salt. The progress of the photoxidation of Cp_2M and the decrease in the CTTS bands of EDA complexes were monitored by UV-VIS spectral measurements.

The quantum yields for the disappearance of EDA complexes (Φ_{CT}) were obtained by monitoring the decrease in the intensity of the CTTS absorptions ($\lambda = 315$ nm for $\{Cp_2Fe \cdot CCl_4\}$; $\lambda = 285$ nm for $\{Cp_2Ru \cdot CCl_4\}$; $\lambda = 278$ nm for $\{Cp_2Os \cdot CCl_4\}$. The photooxidation quantum yields were obtained by monitoring the increase in the intensity of Cp_2M^+ absorptions ($\lambda = 617$ nm, Cp_2Fe^+; $\lambda = 400$ nm, Cp_2Ru^+ and Cp_2Os^+). For the quantum yields determinations the conversions were kept below 10%, and during this part of the reaction a plot of the degree of conversion against the irradiation time is linear. Since only CTTS bands are involved in the reaction, the apparent quantum yields based on the total absorptions are corrected to give the yields based on the absorption by EDA complexes [2,3].

ESR experiments

ESR spectra were recorded with a Bruker ER 200D spectrometer.

The photolysis of EDA complexes in the presence of the spin-trapping agent was performed with solutions in quartz ESR tubes exposed to a Bruker medium-pressure Hg source at the chosen temperature. Corning glass filters were used to ensure selective and specific CT excitation of the EDA complexes. In a typical experiment a degassed CCl_4 solution containing 2.10^{-3} *M* of Cp_2M and 2.10^{-3} *M* ArNO was irradiated at 366 nm in the ESR cavity.

Results

I. When Cp_2M (M = Fe, Ru, Os; Cp = C_5H_5) are dissolved in a halocarbon solvent RCl (CCl_4, $CHCl_3$, CH_2Cl_2, C_2Cl_4) the colour of the CTTS complex is immediately apparent. The CTTS complexes persist in halocarbon solvents for many hours at room temperature if the solutions are carefully shielded from light. The CTTS spectra of EDA complexes appear as broad absorption bands at different positions from those for the localised transitions of metallocenes [2,3]. The position of the charge transfer band ($h\nu_{CT}$) was found to vary monotonically with the electrochemical half-wave potential for RX reduction [8] (Fig. 1).

II. Photoproducts derived from CTTS excitation

The primary photoproducts are the Cp_2MCl salts (eq. 2) and were usually isolated in good yields from photolyzed solutions. UV irradiation of degassed (25 °C) RCl solutions of Cp_2M rapidly yielded precipitates of the coloured solids Cp_2MCl [2,3]. The Cp_2M species are thermally stable in RCl under the photoreaction conditions. The photoproducts do not readily precipitate out from more polar

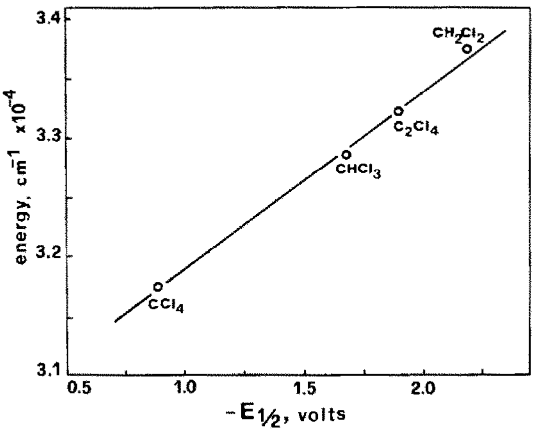

Fig. 1. Correlation of CTTS absorption maximum with halfwave potentials $E_{1/2}$ of halocarbon solvents. $E_{1/2}$ values from Ref. 8.

media [2,3], so quantitative measurements were performed in CCl_4–CH_3OH (75%–25% in v.) (see III).

III. Quantum yields for CT photochemistry of metallocene halocarbon solvent complexes

The quantum yields for the photochemistry of $\{Cp_2M \cdot RCl\}$ complexes was determined by two independent measurements involving the disappearance of the absorption band of the EDA complex (Φ_{CT}) and the formation of the absorption band of the Cp_2M^+ cation (Φ_{ox}) to low conversion (< 10%). The results presented in Table 1 show that $\Phi_{ox} \simeq 2\Phi_{CT}$, and $\Phi_{ox} = \Phi_{CT}$ when an equimolar amounts of a radical scavenger (i.e. PBN) and metallocene are present. This last result is consistent with the consumption of the donor and acceptor in equal amounts directly from the 1/1 EDA complexes (eq. 2). Thus selective excitation of the charge transfer band produced ion pairs (eq. 2) in agreement with Mulliken model for electron transfer upon photoexcitation of the EDA complexes.

$$Cp_2M + RCl \overset{a}{\rightleftarrows} \{Cp_2M \cdot RCl\} \xrightarrow[CTTS]{h\nu} \{Cp_2M^+, RCl^-\}$$
$$\{Cp_2M^+, RCl^-\} \xrightarrow{b} Cp_2MCl + {}^{\cdot}R \qquad (2)$$

The geminate ion pair decays by a process that efficiently generates photoproducts such as the Cp_2M^+ cations, since the quantum yields for Cp_2M oxidation is nearly unity (Table 1). This indicates that the combination of the geminate ion pairs is clearly not competitive with diffusive separation (step b). The final step of the photoreaction involves the interaction of radicals $^{\cdot}R$ with the excess of Cp_2M to produce Cp_2FeCl, Cp_2RuCl, or Cp_2OsCl in high overall yield (Table 1). The results obtained in the presence of radical trap (Table 1) indicate that after the separation of the caged species the free radical $^{\cdot}R$ interacts again with Cp_2M to reform the Cp_2M^+ species.

IV. ESR spin trapping of intermediate radicals

Identification of intermediates $^{\cdot}R$ in reactions initiated by single electron transfer is essential to an understanding of the mechanism of those processes. Selective excitation of CTTS absorption bands of EDA complexes in a rigorously deoxygenated CCl_4 solution of Cp_2M containing nitrosobenzene (ArNO) affords the spin adduct spectrum shown in Fig. 2. The spectrum is quite distinctive, showing the

Table 1

Quantum yields for the photolysis of $\{Cp_2M \cdot RCl\}$ [a] CTTS complexes (λ = 366 nm)

	Φ_{ox}	Φ_{CT}	Φ'_{ox} [b]	Φ'_{CT} [b]
$\{Cp_2Fe \cdot CCl_4\}$ [c]	1.95	0.98	0.98	0.98
$\{Cp_2Ru \cdot CCl_4\}$ [c]	1.3	0.75	0.76	0.75
$\{Cp_2Os \cdot CCl_4\}$ [c]	0.85	0.56	0.56	0.55
$\{Cp_2Fe \cdot CHCl_3\}$ [d]	0.72	0.60	0.62	0.60
$\{Cp_2Ru \cdot CHCl_3\}$ [d]	0.42	0.34	0.36	0.34

[a] $Cp_2M = 2.10^{-3}$ in 75% RCl–25% CH_3OH in v.: solutions deaerated with N_2. [b] Φ'_{ox}, Φ'_{CT} = quantum yields obtained in presence of PBN (= butyl-α-phenylnitrone) 2.10^{-3} *M*. [c] Quantum yields are ±0.01. [d] Quantum yields are ±0.05.

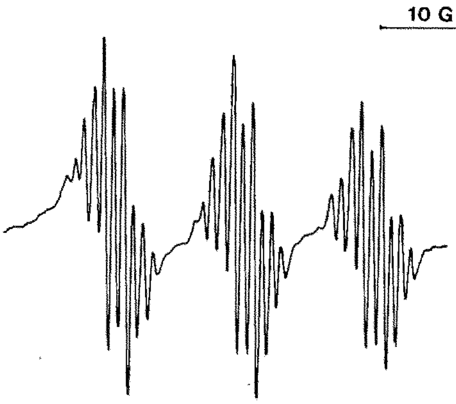

Fig. 2. First derivative X-band ESR spectrum for spin trap nitroxide-radical ArNO + $^{\cdot}\mathrm{CCl}_3$. Hyperfine coupling constant features, $a_{\mathrm{N}} = 13$ G, $a_{\mathrm{Cl}} = 0.98$ G are due to $\mathrm{Ar(CCl_3)NO}$ nitroxide. Degassed $\mathrm{CCl_4}$ solutions containing $\mathrm{Cp_2Fe}$ 2×10^{-3} *M* and ArNO 2×10^{-3} *M*; $\lambda_{\mathrm{exc.}} = 366$ nm. Similar ESR spectra with the same coupling constants were obtained when $\mathrm{Cp_2Ru}$ and $\mathrm{Cp_2Os}$ were used under the same conditions.

features expected for the $\mathrm{ArNO \cdot CCl_3}$ adduct ($a_{\mathrm{N}} = 13$ G, $a_{\mathrm{Cl}} = 0.98$ G), which is stable and can be seen clearly at room temperature. The spectrum of the nitrosobenzene adduct with $^{\cdot}\mathrm{CCl}_3$ showed clear coupling to the three chlorine nuclei (Fig. 2), a feature characteristic of $^{\cdot}\mathrm{CCl}_3$ radicals. Furthermore, in the ESR spectrum of $\mathrm{Cp_2M}$ in $\mathrm{CCl_4}$ in the presence of PBN (Table 2), lines ($a_{\mathrm{N}} = 14.4$ G, $a_{\mathrm{H}} = 1.6$ G) attributable to the $\mathrm{PBN \cdot CCl_3}$ adduct can be unambiguously observed, and the absence of the chlorine atom adduct is evident. It was important to verify this, since our intention was to carry out an experiment aimed at characterizing the radical formed by CTTS photolysis [9].

The data in Table 2 provide present clear evidence for the identities of the radicals $^{\cdot}$R and confirm the operation of the electron transfer process in the systems studied. Because of the rapid formation of the ion-pair, steps (a) and (b) give all the required products, (eq. 2), and thus are favoured as the most likely processes for the EDA complexes formed between $\mathrm{Cp_2M}$ and chlorocarbon solvents.

The data in Table 1 and 2 allow some remarks on the relative reactivities of the halocarbon radicals $^{\cdot}$R towards metallocenes. Of the three radicals $^{\cdot}$R, $^{\cdot}\mathrm{CCl}_3$ is

Table 2

ESR parameters [a]

Radical	Spin trap	Hyperfine coupling constant (G) [b]		
		a_{N}	a_{H}	a_{Cl}
$^{\cdot}\mathrm{CCl}_3$	ArNO	13.0		0.98
$^{\cdot}\mathrm{CCl}_3$ [c]	PBN	14.4	1.6	
$^{\cdot}\mathrm{CHCl}_2$ [c]	PBN	15.2	2.4	
$^{\cdot}\mathrm{CH_2Cl}$	PBN	15.4	3.1	

[a] From ESR spectra obtained after photolysis of $\{\mathrm{Cp_2Fe \cdot RCl}\}$ ($\mathrm{RCl = CCl_4, CHCl_3, CH_2Cl_2}$) EDA complexes in the presence of spin trapping agent. [b] 1 G = 10^{-4} T.

clearly the most reactive. This conclusion is supported by the fact that Φ_{ox} for Cp_2Fe in CCl_4 is higher than Φ_{ox} in the other chlorocarbons.

Under the conditions used the Cp_2Fe complex is the most easily oxidized of the metallocenes studied, and the Φ_{ox} data show that the order of ability of Cp_2M to trap $^{\cdot}CCl_3$ is $Cp_2Fe > Cp_2Ru > Cp_2Os$.

The detection and characterization of transient radical intermediates produced in reactions initiated by CTTS excitation are essential to the mechanistic definition of those processes. The need for such mechanistic understanding is becoming increasingly pronounced in areas of homogeneous photocatalysis and biological electron transfer.

Acknowledgement

This research was supported by the Ministero Pubblica Istruzione. We thank Johnson-Matthey, Inc. for a loan of ruthenium and osmium.

References

1 R. Foster, Organic Charge-transfer Complexes, Academic Press, New York, 1969.
2 S. Sostero, A. Duatti, P. Zanella and O. Traverso, J. Organomet. Chem., 157 (1978) 437.
3 O. Traverso and F. Scandola, Inorg. Chim. Acta, 4 (1970) 493.
4 O. Traverso, S. Sostero and G.A. Mazzochin, Inorg. Chim. Acta, 11 (1974) 237.
5 R.S. Mulliken, J. Am. Chem. Soc., 74 (1952) 811.
6 R.S. Mulliken and W.B. Person, Molecular Complexes: a Lecture and Reprint Volume; Wiley, New York, 1969.
7 M.C.R. Symons, E. Albano, T.F. Slater and A. Tomasi, J. Chem. Soc., Faraday Trans. 1, 78 (1982) 2205.
8 C.K. Mann and K.K. Barnes, Electrochemical Reactions in Nonaqueous Systems, Marcel Dekker, New York, 1970.
9 For authoritative reviews on the use of spin trapping as an investigative tool in electron transfer processes, see: (a) E.G. Janzen; Acc. Chem. Res., 4 (1971) 31; (b) D. Rehorek and H. Hennig, Canad. J. Chem., 60 (1982) 1565.