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Redox reactions via outer sphere charge transfer complexation: the interaction of ferrocenes with σ- and π-type acceptors

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Abstract

Decamethylferrocene Cp^*_2Fe, ferrocene (Cp_2Fe), 1,1′-dimethylferrocene. ($(MeCp)_2Fe$), and 1,2-diferrocenylethane ($Fc_2C_2H_4$) were studied as donors for charge transfer complexation with iodine (I_2) as a typical σ-type CT acceptor and with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), and *p*-chloranil (CHL) as typical π-type CT acceptors. Oxidation of the ferrocenes to the corresponding ferricinium salts is proposed to occur via initial formation of outer sphere charge transfer complexes. UV–Vis spectra for the mixtures of any of the ferrocene donors with I_2 or DDQ in CH_2Cl_2 showed the characteristic bands of the triiodide ion, I_3^- and the $DDQ^{\cdot-}$ anion radical. With CHL, the same behavior occurred only for Cp^*_2Fe to give $Cp^*_2Fe^+$ and $CHL^{\cdot-}$ radicals. Elemental analyses of the isolated solid complexes indicated the formation of [ferrocene]I_3 for ferrocenes and I_2, except for ($Fc_2C_2H_4$) which gave [($Fc_2C_2H_4$)]I_5. Ferrocene–DDQ complexes were 1:1 except for $(MeCp)_2Fe$ and ($Fc_2C_2H_4$) which gave 1:2 complexes. By using *n*-hexane as a non-polar solvent instead of CH_2Cl_2, the CT band of the Cp^*_2Fe adduct has been observed and the formation constant for this CT complexation was found to be 3900 (±500) $dm^3\ mol^{-1}$.

Keywords: Ferrocenes; Redox reactions; CT complexes; IR; UV–Vis spectroscopy

Interesting and important properties of ferrocene moieties have attracted many researchers for extensive studies. Thus, ferrocenes play a fundamental role in many redox-interactions [1] and synthesis of organometallic compounds characterized by biological [2] and optical activities [3]. Further, Ferrocenes are well known by the intra- [4,5] and intermolecular charge transfer [6].

Outer sphere association of metal complexes has been relatively little studied, although Taube [7] showed that a variety of redox reactions of metal complexes proceed by outer sphere association of oxidant and reductant. Understanding and controlling such associations might have useful applications in catalysis and in molecular recognition.

However, we found that photolysis of decamethylferrocene with perfluoroalkanes leads to defluorination to give perfluoroalkenes [8] and postulated that this proceeds via initial formation of an outer sphere charge transfer (CT) complex. The Cp^*_2Fe/per-F–alkane complexes were too weakly bound to be studied directly by UV–Vis spectroscopy, so we have now moved to much powerful acceptors, elemental iodine, a typical σ-acceptor, and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) and *p*-chloranil (CHL), typical π-acceptors. Charge transfer interactions between some ferrocenes, as

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electron donors, and σ- and π-acceptors (I_2, DDQ, TCNE, TCNQ, CHL, etc.) are well-known [9,10], but no CT interactions have been reported for σ-acceptors, such as iodine, with ferrocenes under investigation.

As early as 1966, Brandon et al. [11] reported the ionic nature of the salts formed from Cp_2Fe/DDQ and Cp_2Fe/TCNE, indicating the occurrence of redox reactions. Gebert [12] proposed that Cp_2^*Fe and DDQ yield the ionic salt $[Cp_2^*Fe^+][DDQH^-]$. Recently, Miller [13] reformulated the salt as $[Cp_2^*Fe^+][DDQ^{\cdot-}]$. In the course of our own work, we found that CT complexes can indeed undergo outer sphere charge transfer to give D.A adducts and then undergo complete electron transfer to give the D^+A^- salt.

All ferrocenes, DDQ, and CHL were purchased from Aldrich Co., and used without further purification, iodine was supplied by Alfa and was resublimed. High purity spectral-grade solvents were used (J.T. Baker). Electronic UV–Vis spectra were recorded with a Cary 3E Varian spectrometer with a temperature-controlled cell holder. IR spectra were recorded with a Midac M1200 FT-IR spectrometer. Microanalyses were performed by Atlantic Microlabs, Norcross, GA, USA and Robertson Microlit Laboratories, Madison, NJ, USA.

Equimolar amounts (0.5 mmol) of Cp_2^*Fe or $Fc_2C_2H_4$ and I_2 were dissolved separately in the minimum volume of *n*-hexane and the solutions were warmed and mixed. An immediate deep green (from Cp_2^*Fe) or dark reddish brown (from $Fc_2C_2H_4$) precipitate was collected, filtered, and washed several times with Et_2O. The solid products were recrystallized from CH_2Cl_2-*n*-hexane and dried in vacuo. For the Cp_2Fe and $(MeCp)_2Fe$ cases, CH_2Cl_2 was used as solvent and the solution of the mixtures was refluxed for 1/2 h. On cooling, deep green precipitates, formed in each case, were collected, filtered, and washed several times with Et_2O. The solid products were recrystallized from CH_2Cl_2 and dried in vacuo. Anal. Calc. for $Cp_2^*Fe\ I_3$: C, 33.98; H, 4.28. Found: C, 34.98; H, 4.22. For Cp_2FeI_3, Calc.: C, 21.19; H, 1.78. Found: C, 21.23; H, 1.75. For $(MeCp)_2FeI_3$, Calc.: C, 24.23; H, 2.37. Found: C, 24.55; H, 2.37. For $Fc_2C_2H_4I_5$, Calc.: C, 25.59; H, 2.15. Found: C, 25.06; H, 2.07.

In a simpler modification of a prior route [14], equimolar amounts (0.5 mmol) of the ferrocenes and DDQ were dissolved separately in the minimum volume of CH_2Cl_2 and the solutions mixed giving rise to an immediate color change. The resulting mixtures were refluxed for 1 h. Precipitated solid products were collected, filtered, and washed several times with Et_2O. The solid products were recrystallized from CH_2Cl_2-*n*-hexane and dried in vacuo. Anal. Calc.: for $Cp_2^*Fe(DDQ)$: C, 60.78; H, 5.46; N, 5.06; Cl, 12.81. Found: C, 59.99; H, 5.84; N, 4.55; Cl, 11.77. For $Cp_2Fe(DDQ)$, Calc.: C, 52.34; H, 2.44; N, 6.78; Cl, 17.18. Found: C, 52.34, H, 2.57; N, 6.81; Cl, 17.36. For $(MeCp)_2Fe(DDQ)_2$, Calc.: C, 50.33; H, 2.11; N, 8.38; Cl, 21.22. Found: C, 49.52; H, 2.68; N, 7.29; Cl, 20.04. For $Fc_2C_2H_4(DDQ)_2$, Calc.: C, 53.52; H, 2.58; N, 6.57; Cl, 16.67. Found: C, 53.36; H, 2.78; N, 6.52; Cl, 16.80.

The reaction of the ferrocenes with I_2 in CH_2Cl_2 always led to the formation of salts via electron transfer. All attempts to identify charge transfer band(s) for mixtures of ferrocenes and I_2 in CH_2Cl_2 failed. Instead, the characteristic [15] bands of the triiodide ion (I_3^-) at 292 and 363 nm (Fig. 1) grew in, while the yellow color of the ferrocenes turned to the green color of the ferricinium salts. The electronic spectra of the redissolved solid complexes in MeOH indicate the presence of ferricinium [16] and I_3^- ions [15].

For Cp_2^*Fe/I_2 in CH_2Cl_2, the triiodide bands appeared immediately on mixing indicating rapid interaction, but for Cp_2Fe/I_2, $(MeCp)_2Fe/I_2$ (Fig. 1), and $Fc_2C_2H_4/I_2$, this oxidation took about five to ten minutes. The stoichiometric ratios of these complexations in CH_2Cl_2 were ascertained by applying the continuous variation method [17] which gave a symmetrical curve with a maximum at a mole fraction of 0.40 of the ferrocene donors with I_2, indicating that the complexes are of the form ferrocene–I_3. Early evidence was reported [18] for the transformation of the associative outer complexes to the dissociative inner complexes. The only reaction pathway previously reported [19] for triiodide formation via the interaction of iodine as a σ-acceptor with strong donors is:

$$\underset{\text{donor}}{D} + \underset{\text{acceptor}}{I_2} \rightarrow \underset{\text{outer complex}}{DI_2} \rightarrow \underset{\text{inner complex}}{D^+I \cdot I^-} \qquad (1)$$

$$D^+I \cdot I^- + I_2 \rightarrow D^+I \cdot I_3^- \quad \text{(triiodide complex)} \qquad (2)$$

This pathway requires a lone pair on the donor, not present in the ferrocene case. We believe that the following pathway can better explain the interaction of ferrocene donors with iodine.

$$\text{(ferrocene)} + I_2 \leftrightarrows \text{(ferrocene)} \cdot I_2 \text{(outer CT complex)} \qquad (3)$$

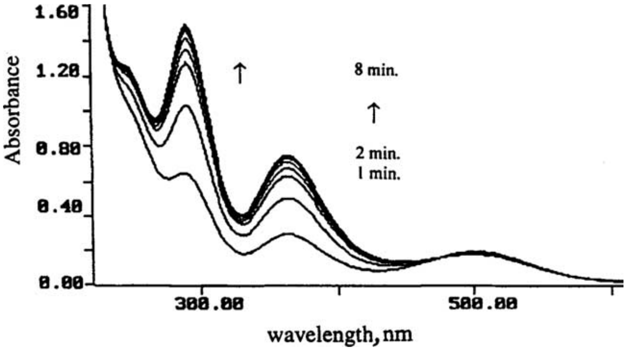

Fig. 1. Effect of time on the electronic spectra of Cp_2Fe/I_2 solution mixture in CH_2Cl_2 at 25 °C; $[Cp_2Fe] = [I_2] = 0.0002\ \text{mol dm}^{-3}$, blank = CH_2Cl_2.

$$(\text{ferrocene}) \cdot \mathrm{I_2} \rightarrow (\text{ferricinium})^{+}\mathrm{I}^{-} + 1/2\,\mathrm{I_2} \qquad (4)$$

$$(\text{ferricinium})^{+}\mathrm{I}^{-} + \mathrm{I_2} \rightarrow (\text{ferricinium})^{+}\mathrm{I_3^{-}} \qquad (5)$$

We propose fast formation of the CT complex followed by a slow step (Eq. (4)) to give the ferricinium ion, followed by formation of triiodide.

Although the system $Fc_2C_2H_4/I_2$ gave both the triiodide and the ferricinium bands in CH_2Cl_2 solution, indicating the formulation $(Fc_2C_2H_4)I_3$, the elemental analyses of the isolated solid complex indicated the formulation $(Fc_2C_2H_4)I_5$; pentaiodide compounds are well known [20]. This formulation implies the presence of one Fe(III) and one Fe(II) in the complex. Accordingly, the solution UV–Vis spectra of $(Fc_2C_2H_4)I_3$ has a shoulder corresponding to the Fe(II) center.

Chlorinated solvents, $CHCl_3$, CH_2Cl_2, and even CCl_4 only gave salts, indeed ferrocenes are known [21] to be oxidized by such solvents. With *n*-hexane, a non-polar solvent, a CT band was formed at 374 nm for the case of Cp_2^*Fe/I_2 at least initially. The donor at the same concentration as in the test solutions was taken as a reference to eliminate any possible interference. Spectra were collected directly after mixing to avoid precipitation which occurred after few minutes for some of these mixtures in the higher concentrations; no thermodynamic data could be obtained in this case. The well known Benesi–Hildebrand plot [22]:

$$[\mathrm{I_2}]/\text{Abs.} = 1/K_{\mathrm{CT}}\varepsilon_{\mathrm{CT}}.1/[\mathrm{Cp_2^*Fe}] + 1/\varepsilon_{\mathrm{CT}}$$
$$(\text{where } [\mathrm{Cp_2^*Fe}] \gg [\mathrm{I_2}])$$

was used to find the association constant (K_{CT}) and extinction coefficient (ε_{CT}). The high values of the association constant, $K_{CT} = 3900$ (±500) $dm^3\,mol^{-1}$ and extinction coefficient, $\varepsilon_{CT} = 1800$ (±200) $dm^3\,mol^{-1}\,cm^{-1}$ indicate that this $n \rightarrow \sigma$ CT complex is of the strong type. This is supported by the ease of transformation into the salt. Because Cp_2^*Fe has only a slightly lower oxidation potential than the other ferrocenes [23], the latter should also give CT bands in hexane, but the incomplete solubility of these ferrocenes prevented their detection.

In CH_2Cl_2, the ferrocenes/DDQ system showed the characteristic bands of the $DDQ^{\cdot-}$ anion radical [24] at $\lambda_{max} = 346$, 435, 458, 546 and 587 nm (Fig. 2). This means that the complexes of these ferrocenes with DDQ exist predominately in the dissociated state: radical cations and anions, D^+A^-. Thus, the recorded spectra of these complexes are perturbed by those of the radical anions, they do not exhibit well defined CT band(s), whereas all attempts to obtain definite CT band(s) did not succeed, and so the determination of the formation constants of these CT complexes is not possible.

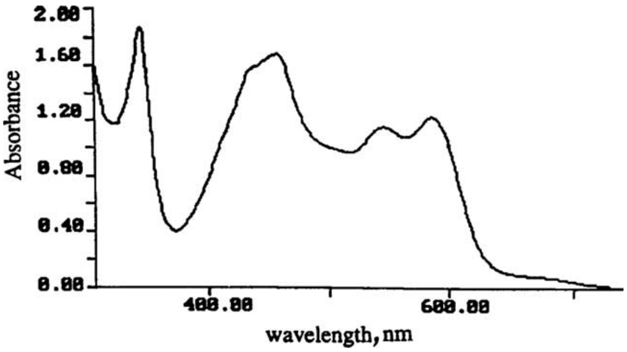

Fig. 2. Electronic absorption spectra of $(MeCp)_2Fe$/DDQ solution mixture in CH_2Cl_2 at 25 °C; $[(MeCp)_2Fe] = 0.001\ mol\,dm^{-3}$, $[DDQ] = 0.0002\ mol\,dm^{-3}$, blank = $[(MeCp)_2Fe]$.

Even though the IR spectra of the isolated solid complexes from the ferrocenes and DDQ are not superimposable on those of the corresponding free ferrocenes and free DDQ, the spectra of the complexes did not exhibit any new bands indicating that no chemical reactions occurred, other than electron transfer from the iron (II) to the DDQ. This suggestion is supported by the following three observations. (a) The complexes displayed the important IR spectral bands of the radical anion $DDQ^{\cdot-}$ [25]; namely, the vibration frequencies of C≡N, C=O, C–C–CN, and C–Cl observed at 2230, 1680, 895, and 803 cm^{-1} for DDQ are shifted to 2198–2216, 1592–1552, 882–852, and 772–728 cm^{-1}, respectively, for the radical anion $DDQ^{\cdot-}$ of the isolated complexes of DDQ with the ferrocene donors. (b) The elemental analyses indicated a 1:1 ratio of Cp_2^*Fe or Cp_2Fe with DDQ and a 1:2 ratio for $(MeCp)_2Fe$ or $Fc_2C_2H_4$ with DDQ. (c) The structural characteristic bands of the radical anion $DDQ^{\cdot-}$ are seen in the UV–Vis spectra along with those of the dark green ferricinium ions. Moreover, we agree with Miller [13] with the formation of the radical anion $DDQ^{\cdot-}$ rather than hydride anion $DDQH^-$ as the result of the interaction of ferrocenes with DDQ.

The CT complexes formed are therefore of the strong $n \rightarrow \pi$ type; i.e., the contribution of the dative structure wave function $Y_{D^{+}-A^{-}}$ in the ground state of the CT complexes is large. In polar solvents, this leads to the complete electron transfer to yield oxidation of Fe(II) to Fe(III); ferrocenes to ferricinium cations via MLCT interaction.

UV–Vis spectral studies also showed the characteristic bands [24] of the $CHL^{\cdot-}$ anion radical at $\lambda_{max} = 425$ and 450 nm, for the mixture Cp_2^*Fe/CHL in CH_2Cl_2, while solutions of the other ferrocene donors in the presence of CHL did not exhibit any new bands. This behavior is consistent with decamethlylferrocene being the most powerful electron donor of the series. Moreover, the ability of DDQ to form complexes with all the ferrocenes in contrast with CHL, which only interacts with decamethylferrocene, is consistent with the higher electron affinity of DDQ [26].

In conclusion, oxidation of organometallic species by halogens is well known, but here we show that in a non-polar solvent, the I_2/decamethylferrocene system forms a charge transfer complex and propose that oxidation occurs via prior CT complexation. DDQ also interacts with ferrocenes to give ferricinium salts of the $DDQ^{\bullet -}$ radical anion.

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