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Preliminary communication

Chemical and Electrochemical Oxidative Cleavage Reactions of Compounds of the Type η^5-$C_5H_5Fe(CO)_2R$

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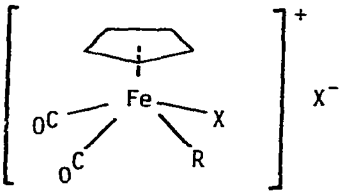
Summary

Chemical and electrochemical one-electron oxidation reactions of η^5-$C_5H_5Fe(CO)_2R$ (R = Me, $PhCH_2$, $PhCH_2CH_2$) in methylene chloride in the presence of added chloride ion yield η^5-$C_5H_5Fe(CO)_2Cl$ and RCl, apparently via the 17 electron complexes, $[\eta^5$-$C_5H_5Fe(CO)_2R]^+$ and η^5-$C_5H_5Fe(CO)_2\cdot$.

Electrophilic cleavage reactions of transition metal-carbon σ bonds are currently generating considerable interest, largely because of the diversity of reaction paths and mechanisms [1]. For instance, in the case of compounds of the type η^5-$C_5H_5Fe(CO)_2R$, cleavage with halogens [2] and mercury(II) salts [3] often appears to proceed via essentially two-electron transfer processes involving formally iron(IV), eighteen electron intermediates such as **1** and **2**.



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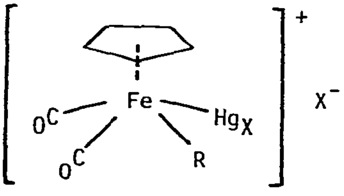

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Table 1. Voltammetric and Coulometric Data

Compound	$(E_p)_a$ (volts)[a]	n (no. of experiments)[b]	Electrolysis Products (yields)[b]
η^5-$C_5H_5Fe(CO)_2Me$	+1.23	0.91 (3)	η^5-$C_5H_5Fe(CO)_2Cl$ (72%)
η^5-$C_5H_5Fe(CO)_2CH_2SiMe_3$	+1.37[c]		
η^5-$C_5H_5Fe(CO)_2CH_2Ph$	+1.28	0.93 (2)	η^5-$C_5H_5Fe(CO)_2Cl$ (79%), $PhCH_2Cl$ (76%)
η^5-$C_5H_5Fe(CO)_2CH_2CH_2Ph$	+1.38	0.93 (3)	η^5-$C_5H_5Fe(CO)_2Cl$ (82%), $PhCH_2CH_2Cl$ (86%)
η^5-$C_5H_5FeCO[P(OPh)_3]Me$	+1.06[c]		
η^5-$C_5H_5FeCO[P(OMe)_3]CH_2Ph$	+0.92[c]		
η^5-$C_5H_5FeCO[PPh_3]CH_2Ph$	+0.80[c]		
η^5-$C_5H_5FeCO[PMePh_2]CH_2Ph$	+0.82[c]		

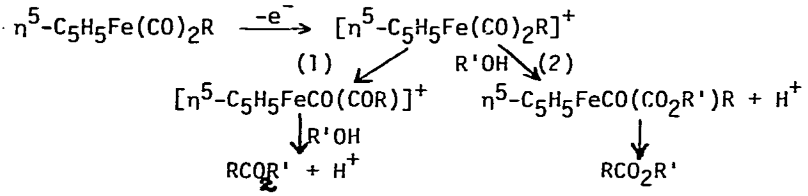
(a) Vs Ag/AgCl (0.1 M Et_4NCl in CH_2Cl_2) reference. Equipment used was a PARC Model 170 Electrochemistry System equipped with a Biomation Model 1015 Waveform recorder. Experiments involved a glassy carbon working electrode, ~3 x 10^{-3} M solutions of complex in deoxygenated CH_2Cl_2, and 0.05 M Et_4NClO_4 (or 0.2 M Bu_4NCl) supporting electrolyte; scan rate 50 mV/sec.

(b) Graphite working electrode, 2.3 x 10^{-3} mole complex, 0.1 M Et_4NClO_4 and 0.1 M Bu_4NCl as supporting electrolyte, in a divided cell. Equipment used was a Wenking electronic potentiostat equipped with a PARC Model 370 Digital Coulometer. Electrolysis potentials were $(E_p)_a$ + 150 mV; n values are corrected for background current.

(c) Coulometry experiments not yet carried out.

Both 1 and 2 can produce a variety of products, although the former preferentially yields alkyl halide.

There have also, however, been a number of reports of cleavage of compounds of the type $\eta^5\text{-}C_5H_5Fe(CO)_2R$ by the typical one-electron oxidants, cerium(IV) and copper(II) [4-6]. When the reactions are carried out using an alcohol, R'OH, as solvent, the major organic product is the ester, RCO_2R', yields decreasing as R' becomes larger. Although few mechanistic data are available, it seems to be generally believed that the initial step is the formation of the seventeen electron intermediate, $[\eta^5\text{-}C_5H_5Fe(CO)_2R]^+$ (3). This could then undergo either rearrangement to an acyl species, which would be attacked at the acyl carbon atom by the nucleophilic solvent with displacement of ester (1), or direct attack at a carbonyl group followed by reductive elimination of ester (2)



$$\begin{tikzcd}
\eta^5\text{-}C_5H_5Fe(CO)_2R \arrow[r, "-e^-"] & {[\eta^5\text{-}C_5H_5Fe(CO)_2R]^+} \arrow[dl, "(1)"'] \arrow[dr, "R'OH\ (2)"] & \\
{[\eta^5\text{-}C_5H_5FeCO(COR)]^+} \arrow[d, "R'OH"] & & \eta^5\text{-}C_5H_5FeCO(CO_2R')R + H^+ \arrow[d] \\
RCO_2R' + H^+ & & RCO_2R'
\end{tikzcd}$$

Either pathway would explain the observed retention of configuration at R [5,6]. Interestingly, chlorine and bromine have been found to yield acyl products under certain conditions, suggesting perhaps that these reagents can function as both one- and two-electron oxidants [6].

In an effort to study the chemistry of species such as 3, we have undertaken a comparative study of both the chemistry of compounds of the type $\eta^5\text{-}C_5H_5Fe(CO)_2R$ with halogens and copper(II) salts, and the electrochemistry, including cyclic voltammetry and coulometry experiments. A similar approach with oxidative cleavage reactions of alkylcobaloxime complexes has proven to be very fruitful [7], and it was hoped that comparison of the products from chemical and electrochemical oxidation experiments run under closely similar conditions would shed some light on the nature of the oxidative cleavage reactions of the iron compounds.

The results of cyclic voltammetry and exhaustive controlled potential electrolysis experiments, all run in dried and purified methylene chloride, are listed in Table 1. Voltammetric experiments in the presence and absence of added chloride ion gave essentially identical results. As expected [8], the ease of oxidation of the compounds η^5-C_5H_5FeCOLR tends to parallel the electron-donating ability of the ligands, while the number of electrons, n, abstracted from each of the dicarbonyl compounds is unity. The initial products of all the oxidations are clearly very labile, as the cyclic voltammetry experiments showed no reduction peaks on the reverse scans, even at scan rates as high as 200 V/sec. Similar experiments in ethanol and acetonitrile gave analogous results.

The coulometric experiments discussed here were carried out in the presence of chloride ion, in part in order to facilitate comparisons with halogenation studies of, for instance, η^5-$C_5H_5Fe(CO)_2CH_2CH_2Ph$ [2], in part because the reactions are less complicated than when run in the absence of chloride ion (see below). Although some decomposition to inorganic iron-containing material occurred, as shown by the yields of products and a coating on the anode which had to be occasionally removed, the reactions were quite clean. Monitoring the three coulometric experiments carried out to this point by infrared spectroscopy revealed only η^5-$C_5H_5Fe(CO)_2Cl$ as an iron-containing product, there being no acyl species detected.

For purposes of comparison, chemical oxidations with $CuCl_2 \cdot 2H_2O$ have also been carried out. Although, as expected [4-6], reactions of both η^5-$C_5H_5Fe(CO)_2CH_2Ph$ and η^5-$C_5H_5Fe(CO)_2CH_2CH_2Ph$ with $CuCl_2 \cdot 2H_2O$ in methanol yielded the esters, $PhCH_2CO_2Me$ and $PhCH_2CH_2CO_2Me$, respectively, reaction of the benzyl complex with excess $CuCl_2 \cdot 2H_2O$ in methylene chloride proceeded essentially as in (3), all yields being based on the amount of iron compound reacted.

$$\eta^5\text{-}C_5H_5Fe(CO)_2CH_2Ph + 2CuCl_2 \cdot 2H_2O \longrightarrow \underset{82\%}{\eta^5\text{-}C_5H_5Fe(CO)_2Cl} + \underset{87\%}{PhCH_2Cl} + \underset{76\%}{2CuCl} \qquad (3)$$

The close similarity in products of the chemical and electrochemical oxidations in methylene chloride, both carried out in the presence of chloride ion, is consistent with the postulate that a common intermediate is $[\eta^5\text{-}C_5H_5Fe(CO)_2CH_2Ph]^+$ ($\underset{\sim}{4}$) (4). As benzylic compounds are generally quite

$$\underset{\sim}{1} + CuCl_2 \longrightarrow \underset{\sim}{4} + CuCl \qquad (4)$$

susceptible to nucleophilic substitution reactions, a reasonable reaction of 4 with chloride ion would involve displacement of the radical, η^5-$C_5H_5Fe(CO)_2\cdot$, from 4 as in (5) [7]:

$$\textbf{4} + Cl^- \longrightarrow \eta^5\text{-}C_5H_5Fe(CO)_2\cdot + PhCH_2Cl \qquad (5)$$

The species η^5-$C_5H_5Fe(CO)_2\cdot$ has been generated photochemically in methylene chloride and readily abstracts chlorine from the solvent to form η^5-$C_5H_5Fe(CO)_2Cl$ [9], the major iron-containing product of the oxidation reactions. The radical would probably also react with copper(II) chloride, however, as in (6) [10]:

$$\eta^5\text{-}C_5H_5Fe(CO)_2\cdot + CuCl_2 \longrightarrow \eta^5\text{-}C_5H_5Fe(CO)_2Cl + CuCl \qquad (6)$$

Reaction (3) is the sum of reactions (4), (5) and (6), suggesting the validity of the postulated steps. The relatively low yield of CuCl, on the other hand, may suggest that some of the η^5-$C_5H_5Fe(CO)_2Cl$ results from reaction of the radical with solvent rather than with the copper(II) chloride. Reaction of the radical with the solvent is presumably the only source of η^5-$C_5H_5Fe(CO)_2Cl$ in the coulometry experiments.

Coulometry experiments with the methyl and phenethyl compounds, η^5-$C_5H_5Fe(CO)_2R$ (R = Me, CH_2CH_2Ph), yielded the same types of products as were obtained with the benzyl compound. Furthermore, coulometry experiments with η^5-$C_5H_5Fe(CO)_2\overset{*}{C}H_2CH_2Ph$, labelled with carbon-13 to the extent of 5%, yielded phenethyl chloride in which the methylene carbon atoms had been scrambled, while similar oxidation of threo-$PhCHDCHDFe(CO)_2(\eta^5\text{-}C_5H_5)$ yielded $PhCHDCHDCl$ with predominant retention of configuration; these are the same results obtained from chlorination experiments [2], suggesting a possible similarity in mechanism. On the other hand, as mentioned above, oxidation with copper(II) chloride in methanol gives ester, while chlorination in methanol gives phenethylmethyl ether [2].

Other complications arise when coulometry experiments are carried out in the absence of chloride ion. Whereas acyl products are absent in the experiments described above, several acyl compounds seem to be produced when electrolyses are carried out using only a perchlorate salt as supporting electrolyte. These and the phenethyl experiments are being investigated further.

Acknowledgements

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