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THE ELECTRON-DONOR PROPERTIES OF FERROCENE

BARBARA FLORIS, GABRIELLO ILLUMINATI, PETER E. JONES★ and GIANCARLO ORTAGGI
Department of Chemistry and Centro C N R dei Meccanismi di Reazione, University of Rome, 00185 Rome (Italy)

The electron-donor ability of ferrocene is suggested by a number of chemical properties, such as charge-transfer complex formation, the high reactivity in electrophilic substitution reactions and the ease of oxidation to ferricinium ions[1]

A fundamental problem related to these properties is the location in the ferrocene molecule of the electron-donating site, which can be the cyclopentadienyl ring (Cp), a functional group attached to it, or the iron atom.

Participation by the non-bonding *3d* electrons of the metal in the reactions of the iron group metallocenes has drawn the attention of several investigators In particular, evidence has been provided for the metal atom to be the site of protonation[2] and of hydrogen bonding[3,4], and, possibly, to act as a neighbouring group in internal electron transfer reactions of α-metallocenylcarbonium ions[5,6], and in the solvolysis of α-metallocenylalkyl acetates[7–11] There is a possibility that the metal atom plays a critical role in electrophilic substitution reactions, as the primary site of electrophilic attack[12,13]. Ring substitution would occur through rearrangement of the resulting cation to a σ-complex, followed by loss of a proton. Although many features of this mechanism are undoubtedly attractive, the supporting evidence was only indirect and qualitative in nature[14] It is worth noting that despite the electron-excessive nature of the cyclopentadienyl rings of ferrocene, as predicted by theory[15,16], their potential basicity has been largely neglected so far in the literature.

A. RING vs IRON BASICITY

Rosenblum and co-workers[2] provided NMR evidence for the protonation of ferrocene at the iron atom as occurring in a BF_3-H_2O system, a medium of markedly high proton-donor ability. In contrast, no protonation was observed when trifluoroacetic acid or conc. sulphuric acid were used as solvents Similar findings were obtained[17] for $WCp(CO)_3H$

Actually, ferrocene undergoes extensive ring protonation under even mildly protic conditions[18]. The UV absorptivity of ferrocene in benzene solution increases in the region of 310–380 nm upon addition of trichloroacetic acid (0 1 *M*) The reaction is fast and reversible, it distinctly precedes oxidation under the stated conditions

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★C N R (Rome) Visiting Fellow 1970–1971

The equilibrium constant for the reaction

$$(Cp_2Fe, H^+) + CCl_3CO_2^- \rightleftharpoons Cp_2Fe + CCl_3CO_2H$$

was determined from the spectral data by the Scott modification of the Benesi and Hildebrand method[19]. This and related K values are reported in Table 1.

TABLE 1

Equilibrium constants for the acid–base interaction of ferrocene and some of its ring-substituted derivatives

Substrate	CCl_3CO_2H–benzene $10^3 \times K$	aq. H_2SO_4 K
Ferrocene	1540 ± 50	
Ethylferrocene	100 ± 10	
1,1′-Diethylferrocene	57 ± 3	
1,2-Diethylferrocene	7.7 ± 0.2	
Acetylferrocene	7.3 ± 0.4	631 [a]
Diferrocenylketone	4.4 ± 0.2	263
1,1′-Diacetylferrocene	20.0 ± 0.2	7245 [a]
α-Ferrocenylethanol	6.1 ± 0.1 [c]	4.4 [b,c]
Diferrocenylmethanol	3.6 ± 0.3 [c]	

[a] Concentration range = 30–60%.
[b] Concentration range = 0–20%.
[c] These data were obtained in this laboratory by G. Cerichelli in connection with related studies.

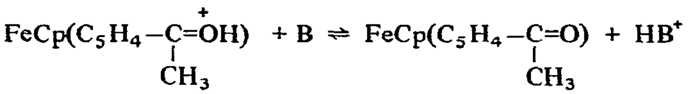
Analysis of the influence of the ethyl groups as a function of their position in the Cp rings shows that ring basicity is enhanced by a factor of about 15 per ethyl group if the groups are located in the same ring. However, basicity increases by a statistical factor of only 2 when an ethyl group is added at the unsubstituted Cp ring of ethylferrocene. These results suggest that in the mildly protic conditions used, protonation occurs at a Cp ring, rather than at the metal, and that the electronic transmission of the polar effects of the substituents through the metal is negligible

Ring basicity is also supported by NMR measurements. The interaction of bromoferrocene (0.163 M) with trifluoroacetic acid (1.07 M) in benzene solution results in a change of the intensity ratio α β . u from 2 2 5 to 2 2 6, α and β being the two pairs of non-equivalent positions (5.77 and 6.28 τ) in the substituted ring and u the five equivalent positions (6.01 τ) in the unsubstituted ring (TMS = internal standard). Thus, bromoferrocene appears to pick up a proton on the side of its unsubstituted ring, in line with the fact that in this case it is the Br-substituted ring which is less basic because of the electron-withdrawing inductive effect of Br. The NMR data indicate that the interaction is reversible, which is in agreement with the UV evidence

The kinetics of H/D exchange have been reinvestigated in this laboratory and have essentially confirmed previously published data[20–22]. Although the exact structure of the ring-protonated species obtained in a mildly acidic medium is still unknown, such a species cannot be a σ-adduct since the observed acid–base interaction is decidedly faster than H/D exchange. However, it may be part of the pre-equilibrium preceding the slow substitution step, in accordance with current views on the mechanism of electrophilic aromatic substitution.

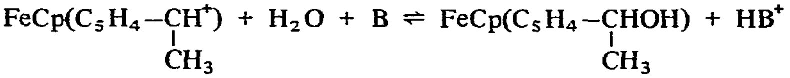
B. α-PROTONATION IN THE SIDE-CHAIN

Carbocations I and II are extensively formed when α-ferrocenyl ketones and alcohols are dissolved in conc. sulphuric acid.



$$\mathrm{FeCp(C_5H_4-\underset{\displaystyle CH_3}{\underset{|}{C}}=\overset{+}{O}H)} + \mathrm{B} \rightleftharpoons \mathrm{FeCp(C_5H_4-\underset{\displaystyle CH_3}{\underset{|}{C}}=O)} + \mathrm{HB^+}$$

I



$$\mathrm{FeCp(C_5H_4-\underset{\displaystyle CH_3}{\underset{|}{C}}H^+)} + \mathrm{H_2O} + \mathrm{B} \rightleftharpoons \mathrm{FeCp(C_5H_4-\underset{\displaystyle CH_3}{\underset{|}{C}}HOH)} + \mathrm{HB^+}$$

II

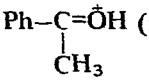
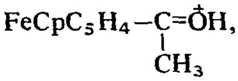
The above reactions have received considerable attention in the course of our studies in connection with the following problems (1) change of the protic medium from aqueous sulphuric acid to trichloroacetic acid in benzene solution, (2) structural effects, and (3) correlation with the solvolytic reactivity of α-ferrocenyl ethyl acetates.

The equilibrium constants for some 30 members of the two investigated series have been determined by UV spectral methods The value available from the literature[23] for carbocation I in aqueous acid was in essential agreement with our measurements Representative data are collected in Table 1.

The CCl_3CO_2H–benzene system displays high proton-donor ability. In fact, the reaction is markedly shifted in favour of the protonated species. The K values for this system appear to be lower than the K values for aqueous acid of any given substrate, however, the former are not strictly comparable with the latter because they are not thermodynamic dissociation constants.

The dissociation constants in the CCl_3CO_2H–benzene system allow a comparison between ring basicity of ferrocene (see preceding section) and side-chain basicity. The fact that the basicity of acetyl ferrocene is greater than that of ferrocene, the factor involved being over 200-fold, indicates that the basic site is *not* the same in the two substrates and confirms the view that acetylferrocene is protonated in the side-chain (carbonyl oxygen). A similar conclusion is arrived at for α-ferrocenylethanol, namely that the protonation site is the side-chain hydroxyl group.

The side-chain basicity is not very sensitive to structural effects. This is dramatically shown by multiple ferrocenyl group substitution. For example, although the

carbocation stability increases enormously on going from $Ph{-}\underset{CH_3}{C}{=}\overset{+}{O}H$ (ref. 24) to $FeCpC_5H_4{-}\underset{CH_3}{C}{=}\overset{+}{O}H$, only a slight increase is noted when $(FeCpC_5H_4)_2C{=}\overset{+}{O}H$ is considered (Table 1).

The iron atom also appears to possess poor ability to transmit polar effects as shown, for example, by the fact that in 1,1′-diacetylferrocene the first dissociation constant is little affected by the unprotonated CH_3CO group located in the other ring, the superimposing influence of field effects being neglected.

Finally, the data for the α-ferrocenyl alcohols yield a linear free energy correlation with the available data for the solvolytic reactivity of α-ferrocenyl acetates. Therefore, the same carbocation intermediates are presumably involved in both reactions, as expected.

C. ELECTROPHILIC REACTIVITY

The aromatic reactivity is one of the most important features of the chemistry of ferrocene. Since oxidation occurs with several reagents, most studies have concentrated on alkylation and, especially, acylation. Nevertheless, a considerable number of other substitution reactions have been successfully applied, thereby providing new routes to a wide spectrum of ferrocene derivatives. They include, to mention some, Vilsmeier formylation[25], Mannich aminomethylation[26], silylation[27,28] and protodesilylation[29], mercuration[27,28,30], and hydrogen exchange[20–22] Relatively little quantitative work has been carried out in this area.

Mercuration with mercuric acetate in acetic acid solution is being studied in our laboratory. The reaction proceeds quite readily and is not affected by oxidation. The reaction can be followed by a UV spectral method and exhibits second-order kinetics, for ferrocene the rate constant is 14 ± 3 $mole^{-1}$ sec^{-1} (uncorrected for the statistical factor). Comparison with similar data with benzenoid substrates[31] shows that ferrocene is 10^9 as reactive as benzene. The rate constant for the mercuration of 1,1′-diethylferrocene is 31 ± 2, which yields a rate effect for the ethyl group (within the same ring) of a factor as low as 2.2.

In analogy with the strong electron-donor molecule hexamethylbenzene[32,33] which reacts with molecular halogen to yield side-chain substitution products, we found that the decamethylferricinium ion reacts with Cl_2 and Br_2 in acetic acid solution[34]. In the case of the latter halogen, UV spectral evidence for the formation of a charge-transfer complex was obtained[35] by the observation of a shift of the absorption maximum of bromine from 400 nm to 480 nm. The kinetics of the halogenation reaction appear to be more complex (Cl_2) than with hexamethylbenzene, the order being two in chlorine.

These results indicate that, despite the rate-depressing effect of the positive charge of the substrate, the latter still retains considerable electron-donor properties in reacting with such mild electrophiles as molecular halogens

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