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THE RING BASICITY OF FERROCENE AND RELATED COMPOUNDS[1]

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The only existing report on the Bronsted basicity of ferrocene concerns the n.m.r. evidence of its protonation at the iron atom[2] which occurs in a BF_3-H_2O system, i.e., a medium of markedly high proton-donor ability. In view of the high electron density of the cyclopentadienyl (Cp) rings, as suggested by both electronic structure and high electrophilic reactivity of ferrocene, ring basicity is expected **Considerable**. Surprisingly, no evidence for such a fundamental interaction has ever been reported so far, although an interaction of this kind **may well be** involved in such reactions as proton exchange[3] and acid-catalyzed oxidation.[4]

We have now found evidence, and obtained quantitative data, for the acid-base interaction of the Cp rings of ferrocene with a mildly protic medium by u.v. spectroscopy. The absorption spectrum of ferrocene changes appreciably in the region of 310 to 380 nm upon addition of trichloroacetic acid (0.1 M) in benzene solution, as the absorptivity generally increases and a slight hypsochromic shift occurs. The reaction is fast as compared to conventional mixing times (< 1 min.); it can be reversed just as quickly back to the reactants on addition of a base (piperidine).

Spectral techniques for the evaluation of equilibrium constants can be applied to the data by assuming the following interaction

$$(Cp_2Fe,\ H^+) + CCl_3CO_2^- \rightleftharpoons Cp_2Fe + CCl_3CO_3H$$

The equilibrium constants (K) were determined by the Scott modification of the Benesi and Hildebrand method[5] for a number of ferrocene derivatives (Table I).

That the measured interaction is not due to the irreversible oxidation to the ferricinium ion, is shown by the fact that it distinctly precedes the latter process; accordingly, the K values are independent of the reactant concentration and wavelength in the stated region. Furthermore, ruthenocene, which is far less sensitive to oxidation than ferrocene, displays an identical spectral behaviour under similar conditions, the equilibrium constant being of the same order as the iron analog (K, 0.48 ± 0.02).

The K values in Table I show that the acid-base interaction is generally enhanced by alkyl groups as predicted by polar effects. However, the effects of the alkyl groups appear to be additive if alkyl substitution occurs at the same Cp ring and statistical if two alkyl groups are distributed between both rings. Accordingly, the increase in K value is about 15-fold on going from the parent compound to the ethyl derivative and from the latter to the 1,2-diethyl derivative; whilst it is only 2-fold on going from the ethyl derivative to any of the 1,1'-dialkyl derivatives. If we assume that the transmission of the polar effect from one Cp ring to another through iron is negligible as compared to that within the same ring, the above results indicate that the K values are a measure of an acid-base interaction involving the Cp ring, rather than the iron atom, as the electron donor. Clearly, in both the ethyl and 1,2-diethyl derivatives the more basic ring is the alkyl-substituted one. These views are in agreement with the finding that the metal is not protonated in the more powerfully protic solvent trifluoroacetic acid.[2]

That the observed interaction provides a measure of ring basicity is also supported by a comparison with the oxidation potentials (Table I, third column). Unlike the K values, the E_{0f} values appear to result from the additivity of the effects of all alkyl groups, no matter how they are distributed between the Cp rings, because the iron atom which is directly

Table I

The Equilibrium Constants (K, at 25°C) for the Acid-Base Interaction of Some Ferrocene Derivatives with Trichloroacetic Acid in Benzene Solution

Ferrocene Derivative	$\underline{K}^a$	$\underline{E}_{of}{}^b$
H	1.54 ± 0.05	-253 ± 6
Ethyl	0.10 ± 0.01	-208 ± 2
1,1'-Dimethyl	0.065 ± 0.005	-149 ± 2
1,1'-Diethyl	0.057 ± 0.003	-160 ± 3
1,1'-Trimethylene	0.045 ± 0.008	-172 ± 2
1,2-Diethyl	0.0077 ± 0.0002	-162 ± 7

[a] Dimensionless.

[b] These data were obtained in this Laboratory by M. Castagnola in connection with related studies. The E_{of} values are in mV vs S.C.E.; sign convention according to W.M. Latimer, "Oxidation Potentials", 2nd Ed., Prentice Hall, New York, N.Y., 1952, for the reaction $Cp_2Fe \rightleftharpoons Cp_2Fe^+ + e$.

involved in the difference in electronic structure between oxidation states, is centrally located relative to both rings.

In view of the possible role of the observed acid-base interaction in the mechanism of H/D exchange, we have reinvestigated the kinetics of this reaction[6] and confirmed previously published data.[3] Since the acid-base interaction we measure is faster than H/D exchange, it cannot consist of a σ-adduct formation and may only be part of the pre-equilibria preceding the slow substitution step. The structure of the protonated species in these pre-equilibria will be the object of further investigations.

References

[1] The content of this paper was read at the V International Conference on Organometallic Chemistry, Moscow, 16-21 August, 1971.

[2] T.J. Curphey, J.O. Santer, M. Rosenblum, and J.H. Richards, J.Am.Chem. Soc., 82, 5249 (1960).

[3] (a) A.N. Nesmayanov, D.N. Kyrsanov, V.N. Setkina, N.V. Kislyakova, and N.S. Kochetkova, Izvestia Akad. Nauk SSSR, Otdel Khim.Nauk, 1932 (1962). (b) J.A. Mangravite and T.G. Traylor, Tetrahedron Letters, 4457 (1967).

[4] M. Aly, R. Bramley, J. Upadhyay, A. Wasserman, and P. Woolliams, Chem.Comm., 404 (1965).

[5] R.L. Scott, Rec.Trav.Chim. Pays-Bas Belg., 75, 787 (1956).

[6] Unpublished work by P.E. Jones.