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MÖSSBAUER STUDIES ON FERROCENE COMPLEXES

XII *. RELATIONSHIPS BETWEEN OXIDATION POTENTIALS AND QUADRUPOLE SPLITTINGS

R.M.G. ROBERTS and J. SILVER

Department of Chemistry, University of Essex, Wivenhoe Park, Colchester, Essex CO4 3SQ (Great Britain)

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Summary

A linear relationship was found between oxidation potentials (measured chronopotentiometrically as quarter-wave potentials $E^{\circ}_{1/4}$ (V)) and ^{57}Fe Mössbauer quadrupole splittings (QS mm s^{-1}) for a series of mono- and di-substituted ferrocenes. This relationship is discussed in terms of molecular orbital energy levels in ferrocenes particularly in respect of the variation of both $E^{\circ}_{1/4}$ and QS with Hammett substituent parameters.

Introduction

The physical and chemical properties of ferrocene have aroused the interests of many theoreticians in the last twenty years. There have been several extensive molecular orbital calculations to account for the Mössbauer parameters of ferrocene and the ferricenium cation.

We briefly summarise the history of the MO treatments here. The first was that of Jaffé [2]. He concluded that free internal rotation should be possible in Cp_2M compounds, estimated the relative energies of the various MO's and suggested that eight electron pairs are principally involved in the metal–ring bonding.

Duntiz and Orgel [3] gave the symmetry properties of the ring and metal orbitals in the D_{5d} symmetry of the molecule.

Moffitt [4] extended the work in two ways: he estimated the relative energies of the metal and ring orbitals and he recognised that the two A_{1g} metal orbitals can mix and that the electrostatic effect of the ring will tend to increase. Moffitt's treatment was still of a qualitative nature and left several important questions unanswered such

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* For part XI see ref. 1.

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as the importance of the interactions between the ring A_{1g}, A_{1u}, e_{1u} and e_{2g} orbitals and orbitals of the same symmetries on the metal. More quantitative work building on that of the earlier workers was then carried out [5–10].

The MO treatments can be simplified and summarized as follows: In D_{5d} geometry the π-orbitals of two parallel C_5H_5 ligands form three sets of nearly degenerate orbitals; a pair of low-lying filled orbitals of a_{1g} and a_{2u} symmetry, a set of filled e_{1g} and e_{1u} orbitals and a high-lying set of antibonding orbitals of e_{2g} and e_{2u} symmetry. These interact with the orbitals of the metal. Of the metal $3d$ orbitals the a_{1g} (d_{z^2}) level is in all cases only very weakly involved in the bonding. The e_{1g} (d_{xz}, d_{yz}) and e_{2g} $(d_{x^2-y^2}, d_{xy})$ orbitals both interact strongly with the ligand π-orbitals, generating an e_1 set which is predominantly ligand-based and an e_2 set which is metal-based.

Mössbauer studies on ferrocene compound are consistent with this bonding arrangement. The collapse of the quadrupole splitting in the ferricenium ion with respect to ferrocene is mainly due to the decrease in Fe $3d_{x^2-y^2}$ and $3d_{xy}$ (e_{2g}) population and a simultaneous increase in Fe $3d_{xz}$ and $3d_{yz}$ (e_{1g}), associated with the removal of one electron from $FeCp_2$.

Trautwein et al. [10] were able to show by inspection of bridged ferrocenes that with increasing number of bridges the valence shell population of iron increases and the quadrupole splitting decreases. They performed MO cluster calculations [11] for ferrocene, ferricenium and bridged ferrocenes to evaluate electron densities at the iron nucleus [12] and electric field gradients [13] and their results compared favourably with experiments.

We have explained in our previous work [1,14–23] how an increase in the *QS* values (i.e. greater than that of solid ferrocene itself) in ferrocene systems is due to electron withdrawal from iron-based orbitals e_2 whereas low *QS* values are due to electron withdrawal via ring based orbitals e_1. In the previous paper [1] in this series we discussed how these ideas could be extended to account for the small *QS* values found for the iron(II) sites and lowered *QS* values (compared to the unoxidised starting materials) for the iron(II) sites of the mixed valence biferrocenium mono cations; and also to account for the lower *QS* vaues (compared to the unoxidised starting materials) for the average valence biferrocenylenium mono cations. Our explanations of the observed Mössbauer data give greater credance to the MO treatments of ferrocene. Partial extra electron density on ferricenium would be expected to and does generate a *QS* (as explained in the biferrocenium mono cations [1]) and removal of this density from ferrocene via e_1 orbitals reduces the *QS*.

In the present paper we present some new correlations of *QS* with oxidation potentials and Hammett parameters for ferrocene derivatives which allow us to extend the theoretical principles outlined above relating ferrocene chemistry to the involvement of HOMO sets e_1 and e_2.

Discussion

The fact that the collapse of the *QS* on oxidising ferrocene is due to removal of one electron, and that partial removal of electron density from a ferrocene moiety causes partially reduced *QS* has led us to speculate as to whether the *QS* is a direct measure or at least a strong indicator of oxidation potential.

TABLE 1

QUADRUPOLE SPLITTINGS (QS mms^{-1}) AND QUARTER-WAVE POTENTIALS ($E^{\circ}_{1/4}$, V) FOR MONO- AND DI-SUBSTITUTED FERROCENES (FcR, FcR_2)

R	QS	$E^{\circ}_{1/4}$ [a]	Ref. for Mossbauer data
CH_3	2.39	0.255	28
H	2.37, 2.40	0.315	17, 26, 27
CH_3CHOH	2.32, 2.36	0.307	17,26
p-$C_6H_4CH_3$	2.36	0.326	29
C_6H_5	2.32	0.346	27
$CON(C_6H_5)_2$	2.31	0.496	29
CO_2CH_3	2.30	0.561	27
p-$C_6H_4NO_2$	2.26	0.443	27
$COCH_3$	2.25, 2.27	0.567	18, 27, 28
COC_6H_5	2.26	0.571	18
CHO	2.24	0.572	29
CO_2H	2.21	0.552	26
$(CO_2H)_2$	2.16	0.768	27
$(COCH_3)_2$	2.15	0.800	18, 20, 28

[a] Data from refs. 23, 24.

To test this hypothesis we have taken the chronopotentiometric data from Little et al. [24,25] and plotted them against a number of QS Mössbauer data. The data plotted from Table 1 appear in Fig. 1 which clearly shows a correlation between the two parameters giving the empirical relationship:

$$QS = -0.42\,E^{\circ}_{1/4} + 2.49 \tag{1}$$

The correlation coefficient is 0.930 for 17 data points. If this plot is extrapolated to a value of QS of 3.09 mms^{-1} (that of $Fe(Cp)_2 \cdot 7HgCl_2$ [14]) a very low value of

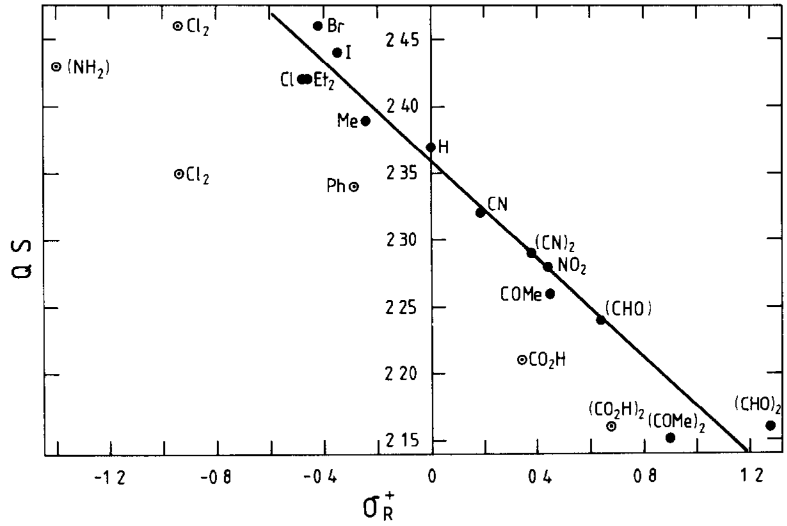

Fig. 1. Quadrupole splitting, QS (mm s^{-1}) vs. quarter-wave potentials, $E_{1/4}$ (V) for substituted ferrocenes (FcR, FcR_2).

$E^{\circ}_{1/4}$ results which is consistent with the observation that the ferrocene-mercury complex undergoes a very ready electron transfer to give a ferricenium derivative. If the plot is examined in the other direction, high values of $E^{\circ}_{1/4}$ are found for the diketones.

It can be seen that these are difficult to oxidise in keeping with experimental evidence. Even in strong oxidising acids, the diketones are very resistant to oxidation (cf. their stability in H_2SO_4 solutions, ref. 18). Additionally, if eq. 1 is applied to ferrocenylcarbenium ions (*QS* values 2.6–2.7 mms^{-1}, refs. 16,17) then very low values of $E^{\circ}_{1/4}$ are predicted which is impossible for positively charged species and again highlights the different mechanism of stabilisation of these ions.

The correlation of oxidation potential with *QS* is dependent on the basic ferrocene unit being essentially identical, i.e. that the rings are parallel and at the same distance from the iron centre. The result of the case where these criteria do not hold is seen in Table 2 for the voltammetric data on bridged ferrocenophanes of Ogata et al. [30]. We have compared this to the *QS* data of Nagy et al. [31–33]. From this data, if the oxidation potentials are plotted against the *QS* values there is no obvious relationship, and if the known crystal structures in the series are examined [34,35] either ring tilting, or the rings being squeezed closer to the iron centre is observed.

Correlations with Hammett constants

In their work on chronopotentiometry of ferrocene derivatives, Little et al. [24,25] reported an excellent correlation of $E^{\circ}_{1/4}$ with Hammett σ_p constants (correlation coefficient $r = 0.995$, 12 data points). Since then other evidence, particularly from NMR studies [36], confirms the use of σ_p values for correlating ferrocene parameters. A much less satisfactory correlation occurs if σ_p^+ values are used ($r = 0.985$) which led Little to the conclusion that resonance contribution of the substituent were

TABLE 2

HALF-WAVE POTENTIALS ($E_{1/2}$, V) AND ELECTRODE POTENTIALS (V) AND QUADRUPOLE SPLITTING (*QS*, mms^{-1}) FOR SOME BRIDGED FERROCENES

Compound [a]	$E_{1/2}$ vs. aq SCE [b]	*QS* [c]	Electrode [d] potential (V)
Ferrocene	0.365	2.367(2)	0.440
[3]FcP	0.300	2.256(3)	0.367
[4]FcP	0.279	2.351(5)	
[3][3]FcP	0.291	2.020(2)	0.359
[4][3]FcP	0.202	2.236(5)	
[4][4]FcP	0.196	2.297(3)	
[3][3][3]FcP	0.292	1.825(3)	0.363
II	0.220 [e]	2.169(3)	0.291
IV	0.200 [e]	1.980(10)	0.270
VIII	0.007 [e]	2.133(2)	0.077
XXII	0.400 [e]	2.236(5)	0.471

[a] Nomenclature of compound same as refs. 30 and 33. [b] D.c. and pulse polarographic data in acetonitrile containing 0.2 mol dm^{-3} TEAP at 25°C from ref. 30. [c] Quadrupole splitting data from refs. 31 and 32. [d] Electrode potentials of bridged ferrocene–ferricenium couples in acetonitrile (22°C, Volt ±0.005) from ref. 33. [e] Data calculated by comparing values from *b* and *d*.

mainly with the Cp ring and were not transmitted directly to the reaction site at the central iron atom. Since $E^\circ_{1/4}$ values appear to vary linearly with *QS*, a correlation of *QS* with Hammett constants was also anticipated. Accordingly *QS* values abstracted from the literature were plotted against a range of constants (see ref. 37 for a current view of substituent parameters). Such a relationship went unnoticed in early Mössbauer studies on ferrocene probably due to one of several factors, viz. lack of wide enough ranges of substituted ferrocene compounds, and poor stability and reproducibility of early Mössbauer spectrometers. Table 3 lists the data for these correlations. *QS* and the inductive substituent constant, σ_I, varied randomly as did *QS* vs. σ°_R, the normal mesomeric constants. However a reasonably good correlation is obtained using σ^+_R (Fig. 2). For this plot the carboxylic acid substituents were omitted in the correlation since inter- and intramolecular hydrogen bonding in the solid phase would alter the value of σ^+_R which was obtained from solutions. In addition, the NH_2, phenyl and dichloro substituents lie off the line. There is uncertainty about the values of mesomeric constant for NH_2 since again it is very

TABLE 3

CORRELATIONS OF QUADRUPOLE SPLITTINGS (*QS* mm s^{-1} at 80 K) AND HAMMETT CONSTANTS [27] σ_p, σ_p^+, σ_I, σ_R and σ_R^+ FOR MONO- AND DI-SUBSTITUTED FERROCENES (FcR, FcR_2)

Monosubstituted ferrocenes						
R	*QS* [a]	σ_p [b]	σ_p^+ [b]	σ_I	σ_R	σ_R^+
H	2.37	0.00	0.00	0.00	0.00	0.00
NH_2	2.43 [c]	−0.66	(−1.3)	0.11	−0.78	(−1.4)
Cl	2.42 [d]	0.23	0.11	0.51	−0.35	−0.47
Br	2.46 [d]	0.23	0.15	0.50	−0.34	−0.42
I	2.44 [d]	0.18	0.14	0.43	−0.23	−0.35
CH_3	2.39	−0.17	−0.31	−0.06	−0.07	−0.24
$CH_3CH(OH)$	2.34 [e]	−0.03	–	–	–	–
C_6H_5	2.34 [f]	−0.01	−0.18	0.10	−0.10	−0.29
p-$CH_3C_6H_4$	2.36 [f]	−0.07 [e]	–	–	–	–
p-$NO_2C_6H_4$	2.26 [f]	0.23 [e]	–	–	–	–
$CON(C_6H_5)_2$	2.31	0.35 [e]	–	–	–	–
CN	2.32	0.66	0.88	0.61	0.00	0.19
C_6H_5CO	2.32	0.46	–	–	–	–
CH_3CO	2.26	0.50	0.84	0.34	0.05	0.45
CHO	2.24	0.52 [c]	1.04	0.35	0.03	(0.64)
CO_2H	2.21	0.45	0.73	0.34	0.03	0.34
NO_2	2.28	0.78	1.24	0.70	0.00	0.44
CH_3CO_2	2.30	0.31	–	–	–	–
Disbustituted ferrocenes						
R	*QS*	σ_p	σ_p^+	σ_I	σ_R	σ_R^+
Cl	2.35 [f] 2.46 [g]	0.46	0.22	1.02	−0.70	−0.94
CN	2.29	1.32	1.76	1.22	0.00	0.38
CH_3CO	2.15	1.00	1.68	0.68	0.10	0.90
CHO	2.16	1.04	2.08	0.70	0.06	1.28
CO_2H	2.16	0.90	1.46	0.68	0.06	0.68
Et	2.42	−0.30	−0.60	−0.12	−0.14	−0.46

[a] Ref. 38 except where indicated. [b] Ref. 39. [c] Ref. 40. [d] Ref. 26. [e] Ref. 24. [f] Ref. 27. [g] Ref. 41.

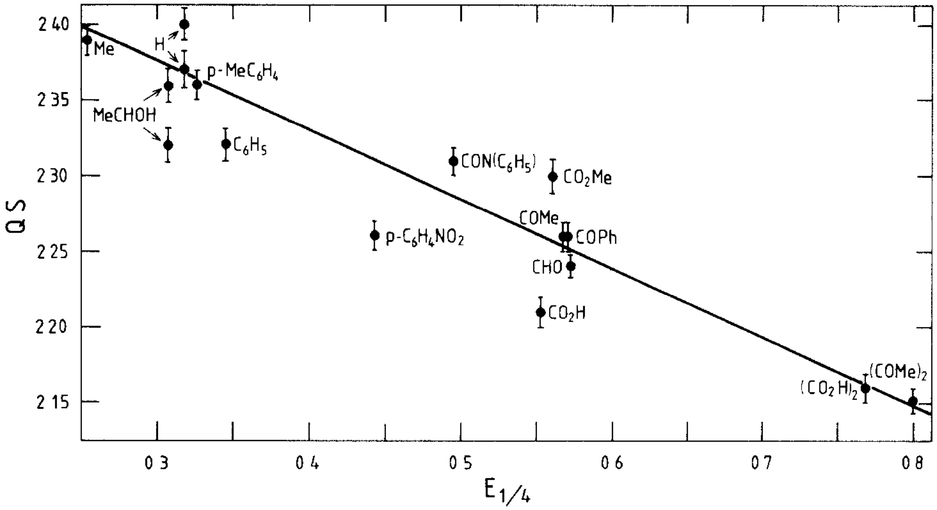

Fig. 2. Quadrupole splitting, *QS* (mm s^{-1}) vs. Hammett resonance constant σ_R^+ for substituted ferrocenes (FcR, FcR_2).

prone to accept hydrogen bonds. Steric hindrance to coplanarity of the Cp and phenyl rings in phenylferrocene would also cause deviation from normal Hammett behaviour. The reason for the anomalous *QS* for the dichloro derivative is unclear and conflicting values for its *QS* have appeared [27,41]. Excluding the above substituents, a correlation coefficient of 0.976 (12 points) is obtained which suggests that resonance involves the partially positively charged iron atom as well as the Cp ring. One other feature of note in this plot is that many of the disubstituted ferrocenes also lie near the correlation line which supports the findings of Little from $E^{\circ}_{1/4}$ measurements that, in heterosubstituted ferrocenes, the substituent effects are additive. We have noted this phenomenon in other systems [18,22]. Plots of *QS* vs. $(\sigma_p^+ - \sigma_p)$ gave a poorer correlation ($r = 0.933$, 12 points) though still clearly indicating resonance involving the iron atom. For the simplest plots of *QS* vs. σ_p and σ_p^+, the latter again provided the better correlation ($r = 0.81$, 24 points and $r = 0.90$, 18 points respectively).

Conclusions

Mössbauer spectroscopy and oxidation potentials although seeming to correlate do in fact measure different electronic properties of the molecule. The *QS* Mössbauer parameter is dependent on the electric field gradient along the molecular axis and usually is governed by electron density changes in the Cp rings which are transmitted by the e_{1g} orbitals. Oxidation potentials ($E^{\circ}_{1/4}$) however are governed by the level of the HOMO orbital in the ferrocene which is generally accepted as being the e_{2g} level. The two orbital sets have very different compositions. The e_2 set comprise about 91% metal-*d* orbital ($d_{x^2-y^2}$, d_{xy}) and only 6.5% ligand orbital character (p_z) whereas the e_1 set has 40% metal-*d* orbital (d_{xz}, d_{yz}) and 53.5% ligand orbital character [42]. Substituent effects on the ring are therefore transmitted mainly via the e_1 orbitals and thus *QS* would be expected to be related to σ_p^+ rather than σ_p. The reverse should be true for $E^{\circ}_{1/4}$, since the iron atom is only weakly conjugated to the Cp rings via the e_{2g} orbitals.

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