THE BEHAVIOUR OF FERROCENE AND RUTHENOCENE IN WEAKLY TO STRONGLY PROTIC MEDIA. IMPLICATIONS ON THE MECHANISM OF SUBSTITUTIONS INVOLVING PROTON AS THE ELECTROPHILE

GIORGIO CERICHELLI, GABRIELLO ILLUMINATI *, GIANCARLO ORTAGGI

Centro C.N.R. dei Meccanismi di Reazione, Istituto di Chimica Organica, Università di Roma, 00185 Roma (Italy)

and ANNA MARIA GIULIANI

Laboratorio C.N.R. di Teoria e Struttura Elettronica e Comportamento Spettrochimico dei Composti di Coordinazione, Via Montorio Romano 36, 00131 Roma (Italy)

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Summary

The interaction of ferrocene and ruthenocene with proton donors has been investigated by NMR spectroscopy in a broad range of protic media, including such weakly protic agents as chloroform, moderately acidic systems such as TFA, and more strongly acidic systems such as conc. H_2SO_4. The results indicate that these metallocenes undergo two kinds of interactions with acidic media, viz., π-hydrogen bonding in which the Cp ring is the electron donor and, in the most strongly protic solvents, metal protonation.

The $(H_0)_{1/2}$ of ruthenocene and a group of ferrocene derivatives have been determined by a combined extractive-spectrophotometric technique. These values show that the metal atom acts as a very weak base. The H/D exchange rate of ruthenocene in conc. D_2SO_4 decreases on increasing acid concentration, which rules out the metal-protonated species as an intermediate in the reaction.

Introduction

The interaction of ferrocene with proton donors has been studied by several investigators. Ferrocene appears to possess two proton-acceptor sites, viz. the metal atom [1] and the cyclopentadienate (Cp) rings [2—5]. The basicity of the metal atom of ferrocene and ruthenocene, which is theoretically justified by the presence of two non-bonding electrons in the equatorial E_{2g} orbital [6], has been proved through NMR investigations of the cations involved in a $BF_3 \cdot H_2O$ medium [1,7]. The role of iron protonation and, more generally, of the iron-electrophile interaction in the reactions of ferrocene has been stirred in several

instances [8—11], but may have been overemphasized when not supported by direct quantitative evidence. There is evidence showing that such a role is not important under certain conditions [12—14].

The electron-donor properties of the Cp rings of ferrocene toward protic agents, which are consistent with molecular orbitals treatments [15—17], have been demonstrated in some instances by electronic [2], IR [3,4], and Mössbauer spectroscopy [18], by dipole moment measurements [19], and by crystallographic determinations [20]. However, the dependence of the two different interactions of ferrocene with protic agents, on the proton-donor ability of the medium has remained still largely unknown. Following previous communications in the field [1,21—23], the studies described below enable us to make a better assessment of this problem.

We have investigated a broad range of protic media, including such weakly protic agents as chloroform, a number of moderately acidic systems such as TFA/benzene or TFA/toluene, neat TFA, and 50 to 72% H_2SO_4, and the more strongly acidic systems 72—96% H_2SO_4, H_2SO_4/TFA (1 : 2.7 molar ratio), and $BF_3 \cdot H_2O$/TFA (1 : 2 molar ratio). The study was based on NMR and, in some cases, electronic spectra measurements.

The $(H_0)_{1/2}$ values for the metal protonation of ferrocene, of some of its derivatives, and of ruthenocene were obtained by a combined extractive spectrophotometric method.

It is convenient to note at this point that evidence will show that H/D exchange at the Cp rings of such metallocenes as ferrocene and ruthenocene does not require a metal—proton pre-equilibrium, in agreement with previous suggestions for protodesilylation and protodeboronation [24].

Results and discussion

Spectral investigation of the effect of protic media
The interaction of weakly protic reagents, such as phenol, phenylacetylene, and chloroform-*d*, with ferrocene and some alkylferrocenes in CCl_4 solution has been studied by IR spectroscopy [3,4], and interpreted in terms of H-bonding involving the Cp ring of the metallocene as the π-electron donor. The H-bonding involving electron-donating π-orbitals has also been discussed [25—27].

Our present NMR results (Table 1) on the chloroform/ferrocene system in CCl_4 support the above interpretation. The interaction is revealed by an upfield shift of the C—H resonance for chloroform in the presence of the metallocene; the shift is in the same direction as observed for the chloroform/benzene system [28] under similar conditions. The upfield shift has been attributed to the highly anisotropic magnetic susceptibility of the electronic π cloud, whereby a proton approaching the ring from above the ring plane finds itself in the screening region of the molecule (Fig. 1a). It is of interest that the shift of the chloroform resonance is to lower field when acetylferrocene is the electron-donor, since in this case the hydrogen-bonding interaction involves the carbonyl oxygen and not the cyclopentadienyl ring. The NMR data were used for the determination of the equilibrium constant for the H-bonding association by the procedure reported by Slejko et al. [29].

Although the changes in resonance frequencies of chloroform are substantial-

TABLE 1

NMR DATA FOR THE ELECTRON DONOR—CHCl$_3$ ASSOCIATION IN CCl$_4$ (T = 25°C; [CHCl$_3$] = 1 X 10^{-2} M)

Donor	K(M^{-1})	$\Delta\nu$(Hz) ^{a,b}
Ferrocene	1.1 ± 0.1	14.2 ± 3.9
1,1'-Dimethylferrocene	1.03 ± 0.09	518 ± 215
1,1'-Diethylferrocene	0.90 ± 0.09	104 ± 27
Acetylferrocene	0.94 ± 0.04	−43 ± 15
Benzene	0.03 ± 0.01	17.7 ± 4.1
Mesitylene	0.28 ± 0.04	19.0 ± 10.0

^{a} $\Delta\nu = \nu_b^{CHCl_3} - \nu_f^{CHCl_3}$, as obtained by the method of Slejko et al. [29], where $\nu_b^{CHCl_3}$ is the resonance frequency of CHCl$_3$ complexed with the electron donor in the ratio 1 : 1 and $\nu_f^{CHCl_3}$ is the resonance frequency of the free chloroform. ^{b} Positive signs correspond to upfield shifts at increasing concentrations of the electron donor.

ly smaller than those found for benzenoid π-electron donors, the association constants for ferrocene and alkylferrocenes turn out to be larger than those for benzenoid donors (Table 1). This is not surprising in view of previous observations that association enthalpies for benzenoid electron donors fail to correlate with either NMR chemical shifts or C—D IR stretching frequencies [29]. Lack of correlation with the free energies of association would be implied in the present case. Also for the intramolecular hydrogen bonding interactions of the OH group of ferrocenyl alcohols to the metal atom and to the Cp ring no correlation of the enthalpies with the IR stretching frequencies was observed [5].

Another group of results concerns the interaction of carboxylic acids, CCl$_3$COOH and CF$_3$COOH, which we refer to as TCA and TFA, respectively, with metallocenes in aromatic hydrocarbons (benzene, toluene, and their deuterated analogs). The use of such solvents was required by our attempts to repeat an early study [30] which appeared to be in doubt [31,32]. Although sys-
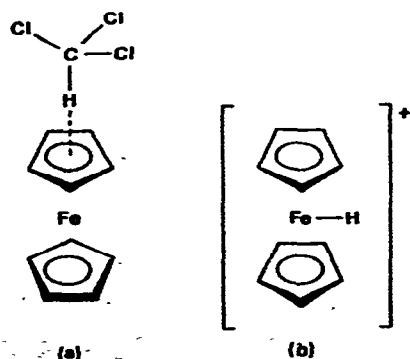

Fig. 1.

tems of this kind contain association equilibria of the protic agent with the added metallocene as well as the solvent, the interaction with the metallocene may still be experimentally distinguishable and susceptible to semi-quantitative investigation.

In a previous paper [2] we studied the interaction of TCA with ferrocene (Fc) and its alkyl derivatives in benzene solution by recording the UV spectral changes in the 310—380 nm region *. We excluded a σ-adduct structure for the complex

$$(TCA, Fc) \rightleftharpoons TCA + Fc$$
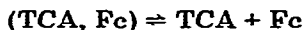
(TCA, Fc), and now we suggest that the weak interaction recorded in that spectral range is likely to correspond to a H-bond association of TCA with the π-electron donor, of essentially the same nature as that already found with $CHCl_3$, phenol, and phenylacetylene. Occurrence of any metal-protonation in mildly protic media is unlikely from these data, since no spectral change is found in the visible region in which the absorption is related to the electronic structure of the metal [33].

We sought NMR evidence to confirm our interpretation of the UV spectral data for similar solvent systems (TFA/aromatic hydrocarbon) by examining ferrocene and ruthenocene, the latter being a more convenient substrate because it is oxidized less easily under the conditions used. In toluene-d_8 solution and in the TFA concentration range 0 to 1 M the spectra of both substrates ($\sim$0.1 M) are unaffected by the acid. The resonance of the Cp rings remains as a sharp singlet. Furthermore, no signal from a proton bonded to metal was observed up to 6 000 Hz upfield from external TMS, from room temperature down to $-70°C$, i.e., even under conditions in which the proton exchange on the metal is expected to be slow enough for unequivocal detection.

For a more detailed investigation, ruthenocene was studied in the TFA/benzene system with cyclopentane as the internal standard. The results indicate that the resonance of the COOH group is shifted upfield when the acid concentration is increased. Since the shift could be due to structure-breaking of the solvent [34] by ruthenocene and not to a specific interaction, a series of NMR measurements was made on TFA solutions in benzene-d_6 but replacing ruthenocene by nitromethane as a structure-breaking agent in the same molar concentration. The data are listed in Table 2. On plotting these frequency data against the TFA concentration, two separate curves are obtained for the solute—solvent systems TFA/benzene-d_6 and TFA/benzene-d_6/ruthenocene; the data for the TFA/benzene-d_6/CH_3NO_2 system fit well into the former curve. Since no shift of the TFA resonance is observed in benzene solution in the whole concentration range examined when nitromethane is added, it seems reasonable to attribute the effect caused by ruthenocene to an interaction of the protic agent with the metallocene [25,29].

The small upfield shift (3.8 Hz) observed for the Cp resonance on increasing the TFA concentration (from 0 to 1 M) does not seem to be significant, as it is comparable to the change in the relative position of the resonances of the cyclopentane reference and of a second internal standard such as TMS, as observed in the same TFA concentration range.

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* In ref. 2 the complex was incorrectly formulated as a dissociated species. Consequently the K values therein reported are in fact in M^{-1} units and not dimensionless.

TABLE 2

INFLUENCE OF RUTHENOCENE ON THE CHEMICAL SHIFTS OF TFA

TFA concentration (M)	Solute—solvent system $\Delta\nu$ (Hz) [a]		
	TFA in benzene-d_6	TFA + 0.1 M CH$_3$NO$_2$ in benzene-d_6	TFA + 0.1 M ruthenocene in benzene-d_6
0.060		419.0	
0.066	419.0		398.5
0.118		501.9	
0.130	503.1		495.2
0.176		557.8	
0.193	566.0		545.5
0.232		587.4	
0.255	594.8		564.5
0.343		623.6	
0.377	633.6		613.9
0.548		672.4	
0.602	681.1		670.2
0.910	722.9		713.2
1.00		727.8	
1.10	736.7		733.0
1.52	765.5		
1.89	782.0		779.2
2.64	803.3		797.4

[a] $\Delta\nu = \nu_{ref} - \nu_{TFA}$; the internal reference is cyclopentane (δ —1.51 ppm from TMS); $\Delta\nu$ values are accurate to ± 0.2 Hz; reproducibility is within ± 2 Hz; $\nu_0 = 90$ MHz; $T = 28 \pm 1°$C.

Even though H-bonding with metal as the electron donor cannot be ruled out in the TFA/benzene system, proton transfer from TFA to iron is excluded by the position of the shifted resonance. Indeed, when a rapid equilibrium between a proton donor and a proton acceptor exists, AH$\cdots$B $\rightleftharpoons$ A$\cdots$HB, the NMR spectrum exhibits only one signal, which is the weighted average of the chemical shifts of the proton in the exchanging sites [27]. The position of the signal, which would be observed if a rapid proton transfer from TFA to ruthenium occurred was estimated on the basis of the equilibrium constant [2] for the TCA—ruthenocene association (K 0.48 M^{-1}) and of the position of the resonance [1] for the ruthenium-bonded hydrogen (1290 Hz upfield from TMS); the upfield shift thus calculated for the TFA resonance, 219 Hz, is far greater than that observed, viz. 8 Hz *.

For the reasons stated above, in the very strongly protonating media ruthenocene was found to be even more amenable to investigation than ferrocene. NMR data in such media and, for comparison, in an aprotic solvent are listed in Table 3. The acidity function, H_0, of the widely different media used was taken as a rough measure of their protonating ability. In neat TFA (H_0 —3.03) [35],

* During the accurate measurements reported in this work we wished to confirm our preliminary NMR data [21] on the interaction of bromoferrocene with TFA in benzene solution, which seemed to provide evidence for a proton transfer from TFA to the unsubstituted Cp ring of the substrate. However, we were unable to duplicate such data.

TABLE 3

NMR DATA ^{a} (δ, ppm) FOR FERROCENE ^{b} AND RUTHENOCENE IN SOME STRONGLY ACIDIC MEDIA AT 28°C

Solvent ^{c}	Ru—H	C_5H_5 (ruthenocene)	Fe—H	C_5H_5 (ferrocene)
Benzene		—3.29		—2.81 ^{d}
CF_3CO_2H (—3.03)		—4.32		—3.44
80% H_2SO_4 (—7.46)		—4.18		
H_2SO_4/CF_3CO_2H, 1 : 2.7 (—9) ^{e}	+8.43	—4.09		
$BF_3 \cdot H_2O/CF_3CO_2H$, 1 : 2 (—11.4) ^{f}	+8.37	—4.20	+3.12	—3.80

^{a} δ Values from internal pivalic acid (δ —1.23 ppm from TMS). ^{b} Data from ref. 1. ^{c} H_0 value given in parenthesis whenever available. ^{d} In CCl_4. ^{e} Value obtained by interpolation [45]. ^{f} H_0 value relative to the $BF_3 \cdot H_2O$ system [46]. It is probably an upper limit.

ruthenocene shows only a sharp singlet at δ —4.23 ppm from pivalic acid and any resonance due to metal-bonded hydrogen is absent. The frequency range examined was from —3 000 to +6 000 Hz from external TMS in the temperature range from —20 to +40°C. In 80% H_2SO_4 (H_0 —7.46) ruthenocene also shows a sharp singlet of the Cp ring at δ —4.18 ppm from pivalic acid. Only in the most strongly protonating media examined, i.e. 90—96% H_2SO_4, $BF_3 \cdot H_2O$/TFA (1 : 2), and H_2SO_4/TFA (1 : 2.7), is metal protonation revealed by an absorption strongly upfield from pivalic acid (δ +8.37 ppm), while the Cp signal remains as a sharp singlet. The reversibility of metal protonation was checked by recording the NMR spectra after dilution of the acid solution.

The above results suggested a detailed examination of the behavior of ruthenocene in H_2SO_4/H_2O mixtures. The NMR data for the system in the range 50 to 96% H_2SO_4 are shown in Table 4; concentrations lower than 50% are unpracticable because of the low solubility of ruthenocene. Over the whole range the ring hydrogens appear as a sharp singlet which is continuously shifted upfield on increasing acid concentration. The metal hydrogen signal appears as a sharp singlet in 96% H_2SO_4; however, it broadens in 90—87% H_2SO_4 and disappears in 85% H_2SO_4. It is of interest that the chemical shift of the Cp singlet in neat TFA is the same as in 72% H_2SO_4 despite the large difference in the corresponding H_0 values; this clearly indicates that the acidity function, H_0, values for varying types of solvent systems may not be comparable to each other and provides a clear example of the limitations in their applications.

Table 3 shows that there is in fact no apparent correlation of the chemical shift of the Cp proton of ruthenocene with the acidity of the media as indicated by the H_0 values. Diverse solvation effects are likely to play a major role in determining the resonance frequencies. Accordingly, in a uniform solvent system, such as H_2SO_4/H_2O, in the acid concentration range 50 to 96% where only a given type of solvation occurs, the Cp resonance shifts regularly upfield (Table 4). It is of interest that in the aprotic solvents used (i.e., benzene and CCl_4, Table 3) the Cp resonance is markedly shifted upfield, even more than in 96% H_2SO_4.

TABLE 4

NMR DATA FOR RUTHENOCENE IN AQUEOUS SULFURIC ACID AT VARYING CONCENTRA-
TIONS ($T = 60°C$)

% H_2SO_4	H_0 [a]	$\delta(C_5H_5)$ [b] (ppm)	$\delta(Ru—H)$ [b]
50	—3.30	—4.50	
55	—3.70	—4.48	
60	—4.37	—4.41	
65	—5.05	—4.29	
70	—5.82	—4.27	
72	—6.13	—4.23	
80	—7.46	—4.18	
85	—8.25	—4.16	+8.35
90	—9.01	—4.10	+8.44
96	—9.98	—4.07	+8.52

[a] Data from ref. 44. [b] Internal reference pivalic acid (δ —1.23 ppm from TMS).

The behavior of ferrocene does not parallel that of ruthenocene exactly. Our data for ferrocene (Table 3) are in essential agreement with those reported by Rosenblum et al. [1].

To sum up, the NMR data unequivocally confirm that ruthenocene and ferrocene undergo two kinds of interactions with acidic media, i.e., π-hydrogen bonding whereby the Cp ring is the electron donor (Fig. 1a) and, in the most strongly protic solvents, metal protonation (Fig. 1b). Further work could be directed toward a better understanding of the relationships between the acid-base equilibria involving the metallocene and the Cp proton and M—H resonances as functions of the acidity of the medium.

We must comment on the electronic spectra. These have also been inspected in moderately and strongly acidic conditions within the limits of experimental accessibility taking into account that ferrocene is easily oxidized in both TFA and H_2SO_4 and ruthenocene slowly decomposes in the same solvents. Electronic spectra are valuable in connection with metal protonation, which is expected to affect markedly the electronic structure of the metallocene. The visible spectra of ferrocene in 5 and 8 M HCl solutions in absolute ethanol (H_0 —1.62 and —2.76, respectively [36]) are nearly the same as those in 96% ethanol, with a limited increase in molar absorptivity in the 320 nm region, which was already observed in the benzene/TCA system [2] and attributed to π-hydrogen bond association (see above). Therefore, as far as these HCl media are concerned, metal protonation of ferrocene can be ruled out since the expected electronic metal transitions would be responsible for marked changes in the visible. As for ruthenocene the absorption maxima fall in the UV region only, at 278 and 320 nm. In $CH_3OH/H_2O/H_2SO_4$ mixtures having compositions from 9 : 1 : 1 to 4 : 1 : 5 by weight, the spectrum remains practically unchanged showing a small increase in the molar absorptivity at the maxima wavelengths. Only in such very highly acidic media as 80% and 90—96% H_2SO_4 marked spectral changes begin to appear. However, they are not reversible on dilution and have not been studied any further.

Determination of the half-protonation H_0 values

The quantitative investigation of the equilibrium for the metal protonation of ferrocene (eq. 1) and related compounds was accomplished by Arnett's meth-

$$(Cp_2Fe-H)^+ + B \rightleftharpoons Cp_2Fe + BH^+$$
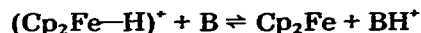
od [37] as based on phase distribution of the substrate between heptane and aqueous sulfuric acid solutions of known H_0 in the range 45 to 96% H_2SO_4 (see Experimental). By such a method we have obtained K'_d and D values, where K'_d is the distribution ratio for the equilibrated base between the organic phase and the aqueous acid of sufficiently low acidity to allow the base be essentially un-protonated, and D the observed distribution ratio in a solution of acidity h_0. The K'_d values were estimated from the intercept of a plot of D vs. Dh_0 and were found to be in the range of 10 to 20, which justifies the use of equal volumes of the organic and aqueous layers in the extraction procedure. In principle pK_a values should be derived from the linear plots of $\log D/(K'_d - D)$ vs. $-H_0$. However, the slopes of these plots (m, Table 5) were found to be consistently different from unity, the value required for a satisfactory Hammett base. Therefore the H_0 value corresponding to $\log D/(K'_d - D)$ equal zero is not a true thermodynamic pK value but, rather, a half-protonation value, $(H_0)_{1/2}$.

The $(H_0)_{1/2}$ values for ruthenocene, ferrocene, and a number of ferrocene derivatives are reported in Table 5. The reproducibility of the $(H_0)_{1/2}$ values was found to be in the range of $\pm 0.3 H_0$ units. In one case, acetylferrocene, the result could be compared with an independent determination carried out by the spectrophotometric method [38]; the two values, -3.2 and -2.8, are in fair agreement to each other.

The data in Table 5 provide the first quantitative estimate of the metal basicity of ferrocene and ruthenocene in solution. They show that metal protonation occurs at very high acidities and that, therefore, the metal atom in these molecules is a very weak base. They confirm our conclusions in the preceding section, viz. that any effect on the Cp proton resonance observed on going from

TABLE 5

HALF-PROTONATION H_0 VALUES FOR THE DISSOCIATION OF METAL-PROTONATED METALLOCENES AT 25°C

$$(Cp_2M-H)^+ + B \rightleftharpoons Cp_2M + BH^+$$
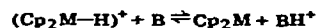
Metallocene	$(H_0)_{1/2}$	m [a]
Ruthenocene	−5.7	3
Ferrocene	−7.7	3
1,1'-Dimethylferrocene	−7.2	2.7
Ethylferrocene	−7.6	3.2
Chloroferrocene	−9.3	2.3
Acetylferrocene	−3.2 (−2.8) [b]	1.4 (1) [b]
1,1',3,3'-Tetra-t-butyl-ferrocene	−8.9	2.8

[a] Slope of the plot $\log D/(K'_D - D)$ vs. $-H_0$. [b] The value in parenthesis was obtained by the (UV) spectrophotometric method.

CCl_4 (or benzene) to CF_3CO_2H solutions cannot be attributed to metal protonation, but rather to a hydrogen bonding interaction with the π-electron cloud of the rings. Within the ferrocene series, the $(H_0)_{1/2}$ values are consistent with the expectations from the polar effects of the substituents, the alkyl derivatives (ethyl and 1,1'-dimethyl) being more basic, and the chloro derivative less basic, than ferrocene. 1,1',3,3'-Tetra-t-butylferrocene is an overcrowded molecule and its low basicity has been attributed to steric hindrance [23]. The relatively high basicity of acetylferrocene is due to protonation at carbonyl oxygen, rather than at the metal [38].

The very low basicity of metallocenes in solution is presumably due to solvation effects, since the basicity of ferrocene is found to be very high in the gas phase, and comparable to that of methylamine [39].

Metal basicity of ruthenocene is found to be higher than that of ferrocene by two H_0 units. Two factors may be invoked to explain this difference. One is the steric repulsion between the two Cp rings, which in the protonated species are no longer parallel but somewhat tilted. This repulsion must be lower for ruthenocene than for ferrocene owing to the appreciably higher inter-annular distance of the former (the values are 3.68 and 3.25 Å, respectively) [40].

Another factor is the extension of the d orbitals, which is more pronounced with ruthenium than with iron, reflecting a general difference between first and second row transition elements [41]. The importance of this factor cannot be predicted with any certainty since crystallographic data for the metal hydrogen distance in the metal-protonated forms are not available. The d orbital extension may give rise to a facilitated interaction of a proton with the donor metal atom in the equatorial position and to a smaller tilting of the Cp rings.

H/D exchange and other electrophilic substitutions

We have already pointed out [24] that such electrophilic substitutions as protodeboronation and protodesilylation are unlikely to receive any significant contribution from an iron-protonated species as an intermediate because they occur in media so mildly acidic as to make the concentration of that species ineffectively small. On the basis of our data on half-protonation H_0 values, the concentration of the metal-protonated species relative to that of the non-protonated species (ionization ratios I) at the acidic conditions used for electrophilic substitutions can be roughly obtained by extrapolation. For the conditions of the protodeboronation reaction (20% H_2SO_4, at 44.7°) and protodesilylation reaction (0.6 M HCl, at 55.2°), the I values were estimated to be as low as 1×10^{-19} and 1×10^{-24}, respectively. These results clearly rule out the intermediacy of the metal-protonated species regarded by some authors as a necessary step in the reaction mechanism [10]. The H/D exchange rate data take this analysis a step further. They indicate that not only is metal-protonation unwarranted but it may, in fact, inhibit the reaction. Some first-order rate constants for the exchange reaction of ruthenocene in aq. D_2SO_4 are reported in Table 6. They include three D_2SO_4 media, 70%, 80%, and 90%, for which the estimated I values for metal protonation are 4.6, 3.5 $\times$ 10, and 1 $\times$ 10^{10} at 25°C. They show that as metal-protonation becomes more extensive the exchange rate falls. Although this analysis is only approximate because truly thermodynamic pK_a values are difficult to obtain, and is carried out with simplifying assumptions

TABLE 6

FIRST-ORDER RATE CONSTANTS FOR THE ISOTOPE HYDROGEN EXCHANGE OF RUTHENO-
CENE IN AQUEOUS D_2SO_4 AT $60°C$

H_0 [a]	k_{obs} (sec^{-1})	
−5.25	$1.5 \pm 0.2 \times 10^{-3}$	
−6.68	$5.5 \pm 0.2 \times 10^{-4}$	
−8.14	$<5 \times 10^{-5}$	

[a] D_0 values are not available for all conditions used. It is assumed that, in the required range, they are es-
sentially similar to the corresponding H_0 values [47].

(neglect of effects of functional group and solvent effects and of differences in
the temperatures used), there is no evidence whatsoever that the metal-protonated
species is an especially reactive intermediate in the exchange reaction.

The deactivating effect of metal-protonation on electrophilic ring substitu-
tion is reasonable in view of the expected electron withdrawing influence of the
positive charge on the Cp rings. Although generated from a different location,
the positive charge in a ferrocenyl carbocation gives rise to a similar effect. Thus,
the cation obtained by complete conversion of 1-ferrocenylethanol in either
neat CF_3CO_2D or 74% D_2SO_4 solution does not undergo any exchange over a
period of days.

In a previous paper [2] we ruled out the possibility that the association species
which is formed from ferrocene in mildly acidic media has the structure of a
σ-adduct, because the rate of exchange is slower than the rate of formation of the
association species. In the first section of this paper we have confirmed this
view by presenting conclusive evidence that only π-hydrogen bonding associa-
tion occurs in mild acids. Combining all the information that has become avail-
able in the course of this and previous studies [2,24] we conclude that the elec-
trophilic substitutions of ferrocene and ruthenocene involving a proton (or
deuteron) as the electrophile (i) do not proceed via a metal-protonated interme-
diate, and (ii) involve a rapidly formed π-complex, which possibly changes over
to an undetected σ-complex, which decomposes to the substitution product. In
other words, we favour a mechanism of essentially the same type as that which
operates in electrophilic substitution of simple benzene derivatives.

Experimental

Materials

Ruthenocene [42] and ferrocene derivatives [43] were prepared as described
in the literature. Commercial ferrocene (Schuchardt) was purified by sublima-
tion. The elemental analyses, melting points, and the infrared, electronic, and
NMR spectra were found to be in good agreement with literature data.

The sulfuric acid solutions were prepared by dilution of 96% H_2SO_4 (Erba RS)
and checked by density measurements and by titrimetric standardization with
NaOH. The H_2SO_4/CF_3CO_2H (1 : 2.7) solvent was obtained by treating 80%
H_2SO_4 with the amount of $(CF_3CO)_2O$ stoichiometrically necessary to use up
the water content of the solution. The $BF_3 \cdot H_2O/CF_3CO_2H$ (1 : 2) solvent was

obtained by treating $BF_3 \cdot 2 H_2O$ (Cationics) with the calculated amount of $(CF_3CO)_2O$. The last two acid systems were not standardized.

The H_0 values recently determined by Johnson et al. [44] were used.

The D_2SO_4 solutions for H/D exchange determinations were prepared by dilution of 96% D_2SO_4 (Merck UVASOL) with D_2O (Merck UVASOL; 99.75% isotopic purity).

Spectral measurements

The NMR spectra were recorded on a Bruker HX-90 spectrometer operating at 90 MHz. Resonances at lower field than TMS are reported as negative δ values. An internal standard (cyclopentane or pivalic acid, δ —1.51 and —1.23 ppm from TMS, respectively) was usually added for reference and for field stabilization; in some cases an external TMS reference was used. The low temperature NMR spectra in deuterated toluene were recorded by use of a Bruker B-ST 100/700 temperature control unit. Temperature values are accurate to $\pm 1°C$; the accuracy on the reading of resonance frequencies is ± 1 Hz.

The samples for NMR measurements were prepared by adding the required amounts of TFA in deuterated benzene or toluene from an Agla microsyringe to a solution of known concentration of the metallocene in the same solvent. The final concentration of TFA was varied from 0 to 1 M.

In the structure-breaking experiments the solutions were prepared by mixing 0.1 M nitromethane in benzene-d_6 and a solution of nitromethane (0.1 M) and TFA (2.6 M) in benzene-d_6 in such ratios as to give a TFA concentration varying from 0.06 to 2.6 M. The NMR spectra of the resulting solutions were recorded and compared with solutions of TFA and ruthenocene in benzene or toluene at the same concentrations.

Ruthenocene solutions in H_2SO_4 for NMR measurements were prepared by weighing ruthenocene (ca. 8 mg) in the NMR tube and dissolving it with 0.5 ml of the solvent.

The electronic spectra of ruthenocene were recorded with a Beckman DB-GT automatic recording spectrophotometer; the concentration of the substrate was ca. $5 \times 10^{-4} M$.

Determination of metal basicity

This was carried out by the combined extractive-spectrophotometric method described by Arnett [37], which has the merit of exposing the substrate to acid media for short contact times (1 min) and, therefore, minimizes acid-catalyzed oxidation of the ferrocene derivatives. A preliminary kinetic investigation in 96% H_2SO_4 at 25°C showed that the first-order rate constants for the oxidation of ferrocene and 1,1'-diethylferrocene are 1×10^{-4} and 1.5×10^{-4} sec^{-1}, respectively; these values are sufficiently low as to make the oxidation during the extraction process quite negligible.

Heptane was first distilled over H_2SO_4 and then over sodium; it was used to prepare stock solutions of the metallocene in such concentrations as to give optical densities in the range of 0.7 to 0.9 (1-cm quartz cells). The initial concentrations (M) of the solutions were as follows (wavelengths, nm, of the investigated maxima given in parentheses). Ferrocene, 8.9×10^{-3} (440); ethylferrocene, 7.6×10^{-3} (438); 1,1'-dimethylferrocene, 5.8×10^{-3} (435); chloroferrocene,

5.6 × 10^{-3} (436); 1,1',3,3'-tetra-t-butylferrocene, 4.5 × 10^{-3} (464); ruthenocene, 1.9 × 10^{-3} (320); acetylferrocene, 3.5 × 10^{-3} (446).

Five-ml aliquots of the stock solution and of aqueous sulfuric acid of known titre in the range 45 to 96% were mixed in a thermostatted cell (at 25°C) with a magnetic stirrer; 1 minute was allowed for equilibration. After complete separation of the two phases, the organic layer was pipetted into the quartz cell and its optical density measured. The observed distribution ratio, $D = [B]_{heptane}/([B]_{aq} + [BH^+])$, was obtained for each compound as the ratio of the concentration of the metallocene in the organic layer to its concentration in the aqueous acid layer after equilibration. These concentrations were obtained as the difference between the absorbance values of the compounds in the starting stock solution and in the organic layer after equilibration. The distribution constants, $K'_D = [B]_{heptane}/[B]_{aq}$, for the free bases were calculated in the region where no protonation occurs and found to lie in the range 10—20. The $(H_0)_{1/2}$ values were evaluated from the straight lines obtained by plotting log $D/(K'_D - D)$ vs. H_0.

Hydrogen—deuterium exchange experiments

The exchange experiments were performed by an NMR method. Ruthenocene was weighed into an NMR tube and dissolved in 0.5 ml of a standard aqueous D_2SO_4 solution. The sample was immediately transferred to the spectrometer and kept at 60°C. The limited solubility of ruthenocene was assisted by the concentration of the acid as well the temperature of the experiment. Integral curves
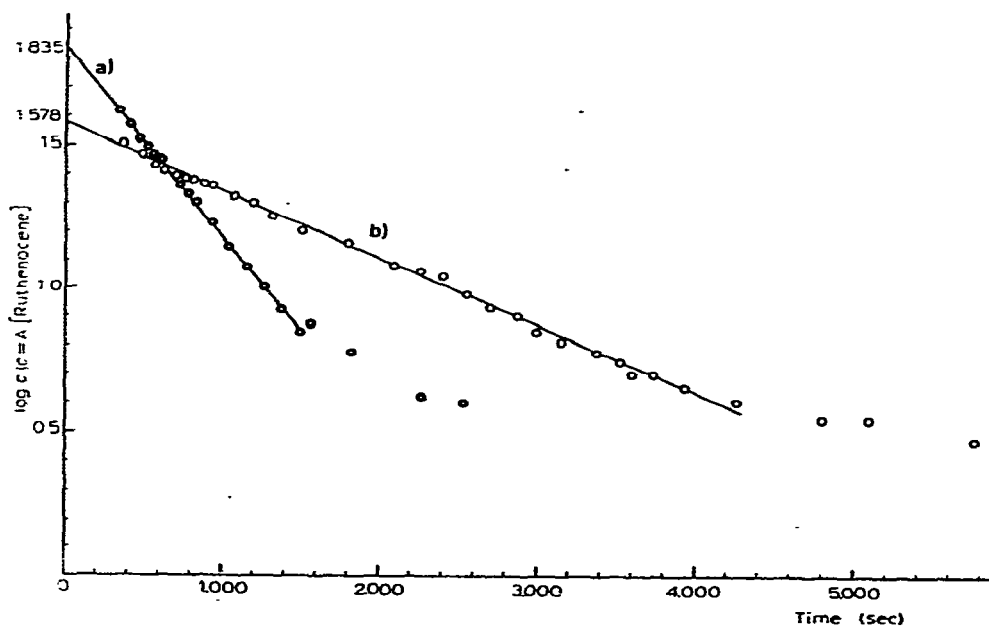

Fig. 2. First-order plot of the H/D exchange of ruthenocene in D_2SO_4 solutions from NMR integral curves. (T = 60°C; a: 70% D_2SO_4; b: 80% D_2SO_4).

were recorded at known time intervals to monitor the decrease of the ruthenocene signal with time. The exchange rate constants were calculated assuming a pseudo-first order process log $(c/c_0) = kt/2.3$, where c/c_0 is the ratio of the ruthenocene concentrations at t and zero time, obtained from the integral NMR curves. Plots of log c vs. t yielded straight lines (Fig. 2), whose slope gives directly $k/2.3$.

Because of the very limited solubility of ruthenocene, the exchange rates of ruthenocene could be determined only at D_2SO_4 concentrations higher than 70%. In 90% D_2SO_4 the exchange, which is negligibly slow, is accompanied by the decomposition of ruthenocene to some unidentified products, which also undergo very slow exchange.

A similar decomposition occurs also in TFA-d_1 solution at room temperature. The decomposition products appear as broad, unresolved resonances at room temperature, but at ca. $-20°C$ they give rise to a singlet (17 Hz downfield of the initial Cp singlet) and two rather broad triplets (111 Hz downfield and 51 Hz upfield of the initial ruthenocene signal). No attempt was made to interpret the nature of these changes.

The exchange of a ferrocenyl carbocation was studied dissolving 1-ferrocenyl-ethanol in 74% D_2SO_4 and recording the NMR spectrum and the integral curve over the course of several days. No variation was observed in the area of the Cp hydrogens relative to that of the methyl hydrogens.

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