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FERROCENYL CARBOCATIONS. THE IONIZATION OF FERROCENYL ALCOHOLS IN AQUEOUS SULFURIC ACID

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Summary

A detailed study of the ionization equilibrium between ferrocenyl alcohols and α-ferrocenyl carbocations in aqueous sulfuric acid has been performed by spectral methods. The spectral characterization of the carbocations, the extent of their formation as a function of the proton-donor ability of the solvent, and the determination of the equilibrium constants are reported. The behavior of ferrocenyl alcohols as indicators compared to that of triarylmethanols is discussed. The transmission of the polar effects of the heteroannular substituents, the heteroannular bridging of an α-hydroxytrimethylene chain, and the high charge delocalization power of the carbocation are also examined.

Introduction

In a preceding paper the protonation of acylferrocenes in aqueous sulfuric acid was discussed and the pK_a values of the corresponding conjugated acids reported [1].

It seemed desirable to extend this study to the ionization of the ferrocenyl alcohols in the same solvent and to the evaluation of the stability constants of the α-carbocations thus formed. Several aspects were expected to be worthy of investigation, such as the comparison with the more familiar triarylmethyl carbocations, the acidity function behavior of the ferrocenyl alcohols, and the assessment of the structural effects of the stability of the α-ferrocenyl carbocations.

While this work was in progress, Nesmeyanov et al. reported the stability constants for a series of heteroannularly-substituted ferrocenyl carbinyl ions in aqueous perchloric acid [2]. The reliability of these results is questioned.

Results and discussion

When the ferrocenyl alcohols are dissolved in neat CF_3CO_2H or in 70—80% H_2SO_4 or in 60% $HClO_4$ solutions, a strong color change is observed, which range from yellow-orange to deep red or purple. By dissolving the alcohols in solutions of increasing sulfuric acid concentration, continuous spectral changes were observed up to a sufficiently high acid concentration. The spectral changes are perfectly reversed on dilution. The aqueous sulfuric acid system was chosen as protonating agent because it is commonly favored in the published studies of the formation of aryl carbonium ions and because the α-ferrocenyl carbocations are remarkably stable in it. In the water/perchloric acid system the spectra change rapidly at any acid concentration and the appearance of an absorption band in the 620 nm region (ferricenium ion) indicates that perchloric acid is probably involved as oxidizing agent. In sulfuric acid solution the electronic and NMR spectra of the α-ferrocenyl carbocations do not change for some days, marked changes being observed only afterwards. It is noteworthy that the carbocations do not decompose in sulfuric acid solutions at sufficiently high concentrations to allow complete formation of the carbocation. For reactions where ferrocenyl carbocations are involved, reference may be made to some recent reports [3. 4].

Structure determination by spectral methods

The formation of carbocations from ferrocenyl alcohols in conc. sulfuric acid or in neat trifluoroacetic acid was unambigously proved by freezing point depression techniques [5]. Although this is probably the most important evidence for the formation of carbocations from the protonated alcohols [6], spectrophotometric and NMR evidence is also valuable.

Our results on the NMR spectra of some ferrocenyl alcohols in $CDCl_3$ and in neat trifluoroacetic acid are reported in Table 1. Unionized 1-ferrocenylethanol in $CDCl_3$ shows the signals of the α and β protons of the substituted ring overlapping with those of the unsubstituted ring as a group of bands at τ 5.8—6.0 ppm. The signal of the methyl group appears as a doublet centered at τ 8.65 ppm and those of the two protons of the CHOH group fall at τ 5.6 (quartet) and 8.3 ppm (singlet), respectively. The position of the OH signal was unequivocally ascertained from its disappearance after shaking in deuterated water. In neat CF_3CO_2H a complete separation of the substituted and unsubstituted ring signals is observed, the signals being at τ 5.0 (singlet) for the unsubstituted ring protons, at 5.4 and 5.6 for the α-protons and 3.7—3.9 for the β-protons of the substituted ring, and at 7.8 ppm for the methyl group; the quartet characteristic of a hydrogen strongly deshielded at τ 3 ppm is attributed to the carbinyl hydrogen of the ferrocenyl carbocation. It is noteworthy that the carbonium ion center causes a predictable strong separation of the proton resonances of the two cyclopentadienyl rings and of the α and β hydrogens of its cyclopentadienyl ring. Analogous behavior is shown by all the ferrocenyl alcohols reported in Table 1. Also, the changes in the NMR spectra of the alcohols and the carbocations therefrom can be interpreted in the same way as that reported previously for ferrocenyl ketones [1]; as expected, a similar mode of charge delocalization is operating in both series of compounds.

TABLE 1

NMR CHEMICAL SHIFTS [τ(ppm)] FOR SOME FERROCENYL ALCOHOLS[a] FeCp(C_5H_4CHOHR)

Ferrocene derivative	in $CDCl_3$						in CF_3COOH						
	H_α	H_β	Cp	R	H	OH	$H_\alpha H_{\alpha'}$		$H_\beta H_{\beta'}$		Cp	R	$^+$CH
Hydroxymethyl	———	5.85	———		5.70	8.38	5.37		3.77		4.83		4.13
α-Hydroxyethyl	———	6.03	———	8.58	5.52	8.23	4.93	5.51	3.63	3.78	4.93	7.73	2.87
α-Hydroxybenzyl[b]	———	6.05	———	2.82	4.8	8.03	4.47	5.10	3.55	3.77	5.10	2.27	1.90
1,1′-Bis(α-hydroxyethyl)[c]				8.59	5.36	4.61	5.05	5.45	3.56	3.7	4.60 4.85	7.7	2.7
α-Hydroxy-1,1′-trimethylene[d]	——	5.5—6.1	——	7.57 8.02		8.24	4.21	5.56	3.47	4.21	3.97 4.95 5.03		1.90

[a] Relative to internal TMS. [b] In CCl_4. [c] The spectrum in CF_3COOH is referred to the monocarbocation. The detailed spectra of the compound are reported in ref. 11. [d] The data in CF_3COOH are from ref. 7.

TABLE 2

SPECTRAL DATA FOR SOME FERROCENYL ALCOHOLS IN DIFFERENT SOLVENTS

Ferrocene derivative	ϵ [cm^{-1} M^{-1} (λ_{max}, nm)]		
	Benzene	Water	H_2SO_4 40—80%
Hydroxymethyl			9,000 (258)
		142 (320)	
		151 (430)	
α-Hydroxyethyl	81 (325)	90 (323) [a]	10,500 (258)
	105 (437)	111 (440)	497 (380)
α-Hydroxybenzyl			10,600 (253)
	163 (300)		12,100 (329)
	111 (437)		3,280 (406)
1'-Ethyl-1-α-hydroxyethyl			10,600 (262)
	150 (434)		570 (378)
1'-Bromo-1-α-hydroxyethyl			8,770 (263)
	153 (442)		
1,1'-Bis(α-hydroxyethyl)			11,100 (263)
		77 (325) [b]	561 (382)
		113 (440)	
1,2-α-Hydroxytetramethylene			9,300 (265)
		124 (440)	595 (380)
α-Hydroxy-1,1'-trimethylene			12,600 (260)
		270 (446)	295 (452)

[a] In ethanol/water, 1/4. [b] In 95% ethanol.

Electronic spectra were only used for the characterization rather than for structural determination, of the α-ferrocenyl carbocations, because the absorption bands of a series of mono- [8] and 1,1'-disubstituted [9] ferrocenes do not correlate with the nature of the substituent in any simple way. This is shown in Table 2, where the absorption data for the alcohols and the corresponding carbocations are recorded. The ferrocenyl carbinyl carbocations show a very strong band in the UV around 250—260 nm with molar absorptivities near 10^4 and a second band in the visible (with the only exception of ferrocenylphenylmethyl cation) with molar absorptivities in the order of 5×10^2. Since the UV band is shown by all the α-ferrocenyl carbocations, it may possess a diagnostic value for this type of compound and arise from the same electronic transitions responsible for the UV spectrum of the protonated ferrocenyl ketones in the same wavelength region [1].

Infrared spectral characterization of all the ferrocenyl alcohols was also performed and it was found to be in very good agreement with the literature data [10]. For some compounds which were not characterized previously by this technique it is convenient to report some structural information useful for the following discussion on the pK_{R^+} values. The IR spectrum of 1,1'-bis(α-hydroxyethyl)ferrocene shows a large band centered at 3320 cm^{-1} and a small peak at 3620 cm^{-1}. Since, in the alcohols of the type $CpFe(C_5H_4CHOHR)$, the frequencies corresponding to the free, π-bonded and Fe-bonded OH groups fall in the region 3618, 3613 and 3580 cm^{-1} [10], the two absorptions of 1,1'-bis(α-hydroxyethyl)ferrocene can be attributed to the free and intramolecularly hydrogen bonded OH groups [11].

The IR spectrum of α-hydroxy-1,1'-trimethyleneferrocene shows a narrow peak at 3620 cm^{-1}. There is no trace of absorption at lower frequencies corresponding to an iron-bonded OH group. This is in agreement with the rigid structure of the compound where the mutual accessibility of the OH and Fe centers is unambigously hindered.

Ferrocenyl alcohols as indicators

Deno and Arnett have discussed thoroughly the behavior of triaryl alcohols in the dehydration process for the determination of the J_o acidity scale [12, 13].

It appeared to be of interest to make a comparison between ferrocenyl and triaryl alcohols as acid—base indicators, in the same way as ferrocenyl ketones were compared to the aryl ketones [1].

We have calculated the quantity $d(\log Q)/d(\%H_2SO_4)$, Q being defined by c_{R^+}/c_{ROH}, for the ferrocenyl alcohols and have found it substantially constant in the range of acid concentration convenient for the pK_{R^+} determination (except in the H_2SO_4 range 2—5%) and identical to those reported for triarylmethyl alcohols in the same acid concentration range [12] (only 1′-bromo-1-α-hydroxyethylferrocene shows $d(\log Q)/d(\%H_2SO_4)$ values from 0.08 to 0.07 in the 16—26% H_2SO_4 range).

However, the close behavior of ferrocenyl and aryl alcohols may be fortuitous, because the ferrocenyl alcohols investigated ionize in a more narrow H_2SO_4 concentration range (2—24%) than Deno's compounds. However, the independence of the term $d(\log Q)/d(\%H_2SO_4)$ for the ferrocenyl alcohols of any particular sulfuric acid concentration indicates that the amount of protonated alcohols in the equilibrium alcohol/carbocation is negligible [12].

The indicator behavior of the ferrocenyl alcohols may usefully be compared with that of ferrocenyl ketones by using a treatment of the data analogous to that reported for the ketones [1, 14] and equivalent to the numerical and graphical methods which had been introduced previously [12, 13]. On the basis of eqn. 1 the plot of log Q vs. J_o must be linear with the slope m equal to unity.

$$J_o = pK_{R^+} - \log_{10}(c_{R^+}/c_{ROH}) \qquad (1)$$

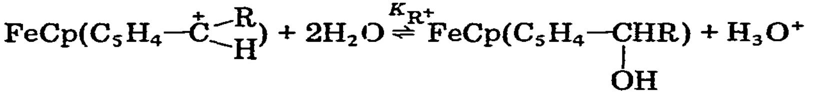
The m values of the ferrocenyl alcohols are reported in Table 3, together with those of the ferrocenyl ketones. The comparison shows that, in fact, the alcohols are poorer indicators than the parent ketones. This must be predominantly due to the differences between the activity coefficients of the "free" carbocation (γ_{R^+}) and of the protonated ketones ($\gamma_{R_2\overset{+}{C}OH}$), because of the markedly different solvation requirements of these charged species. Assuming that the activity coefficients for the alcohols and ketones as neutral species respond in a similar manner to changes in acidity, the differing behavior between the two classes of ferrocenyl bases must depend on changes in the $\gamma_{R^+}/\gamma_{R_2\overset{+}{C}OH}$ ratio for the corresponding charged species and to different states of solvation of the latter [13]. However, it should be noted that the changes in activity coefficients for the alcohols as neutral species may be affected by both π- and σ-intramolecular association of the H-bonding type [10].

The pK_a values

The poor reproducibility of the absorption spectra of ferrocenyl alcohols in aqueous perchloric acid, as described above, led us to question the reliability of the determination of the stability constants of α-ferrocenyl carbocations in this solvent, which was recently reported by Nesmeyanov and his co-workers

[2]. For example, a considerable discrepancy was found for the pK_{R^+} value of 1'-chloro-1-α-hydroxyethylferrocene [2] (—3.39) and that for the analogous 1'-bromo-1-α-hydroxyethylferrocene (—1.52, this work). On repeating Nesmeyanov's work with ferrocenylmethanol and 1-ferrocenylethanol in perchloric acid solutions by the procedure herein described (see Experimental), which involves reduced time intervals (down to 15 sec) between the addition of the acid to the solution of the alcohol and recording the spectrum, we have obtained a significant increase in both pK_{R^+} values and reproducibility. For this reason, the pK_{R^+} determinations were considered to be more reliable in aqueous sulfuric acid (see a preceding section) than in perchloric acid solution.

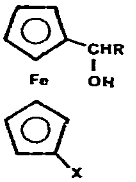
In Table 3 the pK_{R^+} values are reported for the ionization equilibria of a number of ferrocenyl alcohols in aqueous sulfuric acid at 25°C (eqn. 2).



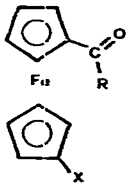
$$\mathrm{FeCp}(C_5H_4-\overset{+}{C}\langle^{R}_{H}) + 2H_2O \overset{K_{R^+}}{\rightleftharpoons} \mathrm{FeCp}(C_5H_4-\underset{OH}{\underset{|}{CHR}}) + H_3O^+ \qquad (2)$$

These data confirm the extraordinarily high stability of the α-ferrocenylcarbonium ions, in agreement with the results obtained on protonation of acylferrocenes. This conclusion is clearly illustrated by the comparison of the pK_{R^+} values of ferrocenylmethanol (—1.49) and ferrocenylphenylmethanol (+0.4) with those of related aralkyl alcohols (2,4,6-trimethylbenzyl alcohol [16], —17.3, diphenylmethyl alcohol [12], —13.3, and triphenylmethyl alcohol [12], —6.63), the stability of triarylmethyl carbocations being of the same order of magnitude only in the presence of strong electron-releasing groups (4,4',4"-trimethoxytriphenylmethanol [12], +0.82).

It may be of interest to compare the structural effects on the basicity of the ferrocenyl alcohols (I) to those for the corresponding ketones [1] (II). A free-energy plot for the available data is reported in Fig. 1. Such data include



(I)



(II)

three heteroannular substituents (X = 1'-H, 1'-Br, and 1'-C_2H_5), a homoannular bridge, 1,2-tetramethylene, a heteroannular bridge, 1,1'-trimethylene, for the series with R = CH_3, and the unsubstituted member for the series with R = C_6H_5. A fairly good linear correlation is obtained for the heteroannular substituents with a slope of 1.07 and a correlation coefficient of 0.98, indicating a very similar sensitivity to structural changes in the two series. Despite the limited number of points at hand, the validity of this conclusion is supported by the fairly wide range of the related pK_a values (about 1.4 pK_a units) by the generally normal behavior of the substituents involved [17], and by the fact that, for a still wider range (2.2 pK_a units), an excellent $\rho\sigma_m$ relationship was found for the basicity of the ketones [1]. The correlation for the alcohols could not be extended to such groups as 1'-$COCH_3$, 1'-CN, and 1'-CO_2H because of difficulties in the determination of reliable equilibrium constants (see Experimental).

TABLE 3

pK_{R^+} VALUES FOR THE HYDRATION OF FERROCENYLCARBOCATIONS IN AQUEOUS SULFURIC ACID AT 25°C

Ferrocene derivative	$10^{-1} K_{R^+}$	pK_{R^+}	% H_2SO_4 at half-ionization	m_{R^+} [a]	$m_{C=O}$ [b]
Hydroxymethyl (I)	310	−1.49 ± 0.08	16	0.79	
α-Hydroxyethyl (II)	44	−0.64 ± 0.10	9	0.90	1.00
α-Hydroxybenzyl (III)	4	+0.4			0.99
1′-Ethyl-1-α-hydroxyethyl (IV)	14	−0.13 ± 0.03	6	0.85	0.98
1′-Bromo-1-α-hydroxyethyl (V)	330	−1.52 ± 0.20	16	0.57	0.47
1,1′-Bis(α-hydroxyethyl) (VI)	560 [c]	−1.75 ± 0.10	16	0.74	
1′-Ammoniomethyl-1-α-hydroxyethyl (VII)	1.7×10^9	−10.2	65		
1,2-α-Hydroxytetramethylene (VIII)	6.3	+0.2 ± 0.04	3.5	0.72	0.99
α-Hydroxy-1,1′-trimethylene (IX)	1.6×10^4	−3.20 ± 0.20	26	0.68	0.96

[a] Slope of the plot of log Q vs. J_0. [b] Slope of the plot of log I vs. H_0 for ferrocenylketones [1]. [c] Corrected value for the statistical factor and referred to the mixture of *meso* and racemic stereoisomers.

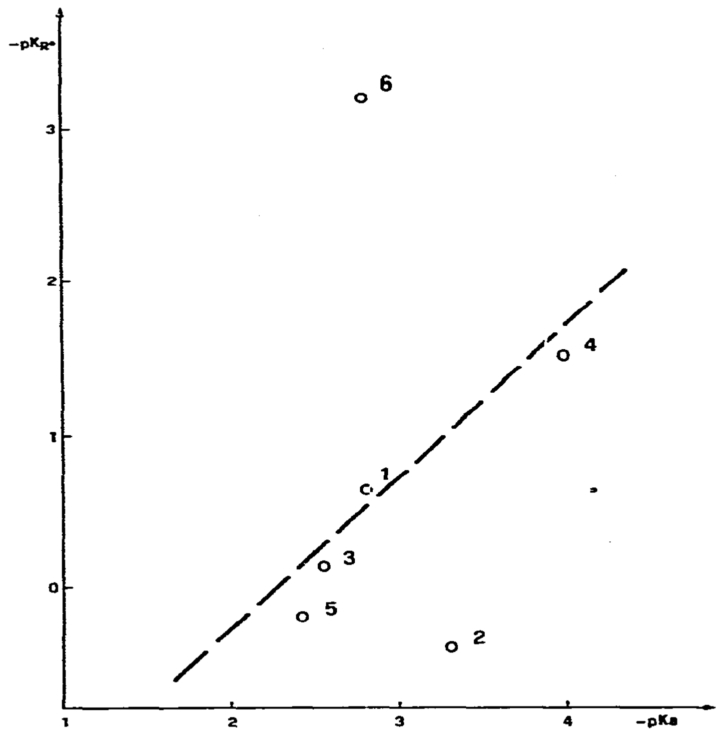


Fig. 1. Plot of pK_{R^+} of ferrocenyl alcohols $Fe(C_5H_4X)(C_5H_4CHOHR)$ vs. pK_a of ferrocenyl ketones $Fe(C_5H_4X)(C_5H_4COR)$: (1) R = CH_3; X = H. (2) R = C_6H_5; X = H. (3) R = CH_3; X = C_2H_5. (4) R = CH_3; X = Br. (5) R = $(CH_2)_3$; X = H (homoannular bridge). (6) R = X = $(CH_2)_2$ (heteroannular bridge).

For the remaining points of Fig. 1 the wide scattering that is observed is not surprising since the corresponding compounds involve direct changes at the reaction sites of the alcohols and ketones. Major differences in behavior are worthy of some comments in connection with the carbocation character of the conjugate acid. One such difference is the fact that, in the case of the alcohols (series I) the basicity is greater for R = C_6H_5 than for R = CH_3 (ΔpK_a 1.04) whereas the opposite is true (ΔpK_a 0.51) in the case of the ketones (series II). This would indicate that the α-carbon (conjugate acid) for series I has a greater carbocation character than that for series II, the electron deficiency being shared in the latter case with the protonated carbonyl oxygen. This view is supported by the greater enhancement in carbocation stability which is observed on going from benzyl alcohol to ferrocenylmethanol (at least 15 pK_{R^+} units) relative to the pair acetophenone—acetylferrocene (5 pK_a units) [1]. Also, a far greater sensitivity to steric inhibition of resonance is experienced by the carbocation from the ferrocenyl alcohol than that from the ferrocenyl ketone since a 1,1′-trimethylene bridging is much more basicity depressing in the alcohol, provided that similar deviations from coplanarity of the carbon with the Cp ring is involved in both cases.

An astonishingly large effect of the 1′-$CH_2NH_3^+$ (Table 3) lowering the carbocation stability by nearly ten powers of ten seems to be caused by the positive charge of the substituent possibly involving an important field effect component in view of the special geometry of the system and the stabilizing influence of intramolecular H bonding on the unionized alcohol. It is also worth noting that the pK_{R^+} constant for the first ionization of 1,1'-bis(α-hydroxyethyl)ferrocene is lower than that predictable on the basis of the polar effect of the heteroannular $CHOHCH_3$ substituent. As suggested above, this must be due to the hydrogen bonding interaction between the two ring substituents, which has been investigated in detail elsewhere [11]. In agreement with the possible charged-substituent effect, it is worth noting that the pK_{R^+} constant for the second ionization of 1,1'-bis(α-hydroxyethyl)ferrocene, which is related to the charged $\overset{+}{C}HCH_3$ group, is immeasurably small.

Correlation with solvolysis rates

Deno [18] found that the pK_{R^+}'s for diarylmethanols correlate linearly with the solvolysis rates for the corresponding diarylmethyl chlorides, the slope of the line being close to unity. A similar relationship is now found for all the available data when the log *k*'s for the solvolysis of ferrocenylalkyl acetates [19, 20] are plotted against the pK_{R^+}'s of the alcohols. The slope is 1.12 and the correlation coefficient 0.98. The pK_{R^+} data include the alcohols II—V and VIII (Table 3); the solvolysis data are for the corresponding acetates except for the 1'-alkyl substituent which was methyl instead of ethyl as with alcohol IV. The existence of such a correlation is in agreement with Hill and Richard's evidence that the mechanism for the solvolysis of the α-ferrocenylethyl acetate series is the same as that of trityl acetate and indicates that in both reactions an intermediate carbocation is formed. It is interesting to note, however, that the rate constants at 30° for these compounds, 1.7×10^{-4} s^{-1} (methylferrocenylcarbinyl acetate), and 2.58×10^{-5} s^{-1} (trityl acetate) are of the same order of magnitude and do not parallel the pK_{R^+} values of the corresponding alcohols, the α-ferrocenylethyl carbocation being more stable than trityl by several powers of 10 (pK_{R^+}, —0.66 and —6.63, respectively). This may indicate that the transition states for the solvolysis of the two acetates differ significantly in degree of carbocation character. If this is the case, the slopes of the abovementioned plots are not a measure of the carbocation character of the activated complex in an absolute way even though their physical meaning is probably similar to that of the so-called α parameter [21].

Experimental

Most ferrocenyl alcohols were prepared by the reduction of the corresponding ketones with $LiAlH_4$ according to previously described procedures [22, 23] and checked by elemental and spectral analysis.

1'-Aminomethyl-1-α-hydroxyethylferrocene and 1'-carboxy-1-α-hydroxyethylferrocene were prepared by reduction with $LiAlH_4$ and $NaBH_4$, from 1'-cyano-1-acetylferrocene and 1'-carboxy-1-acetylferrocene, respectively.

exo-α-Hydroxy-1,2-tetramethyleneferrocene was identified on the basis of the assigned OH IR absorption bands at 3618 and 3603 cm^{-1} [10].

All reagents were spectrophotometric-grade commercial samples.

The instruments and conditions for the measurements were as follows. (1) NMR Jeol C—60 HL spectrometer; measurements in the concentration range of the samples 0.1—0.2 *M* at room temperature. (2) Beckman IR 20 spectrophotometer; measurements in CCl_4 solutions. (3) UV and visible apparatus: Beckman DU spectrophotometer and/or Perkin—Elmer 402 self-recording spectrophotometer; the cell compartment was thermostatted at 25.0 ± 0.1°C; 1-cm silica cells with teflon stoppers were used. (4) A Radiometer PHM 22r pH-meter was used for potentiometric titrations at room temperature.

For the pK_{R^+} determinations the aqueous sulfuric acid and perchloric acid solutions were prepared from 96% sulfuric acid (Erba RS) and 70% perchloric acid (Erba RS) and standardized according to the methods described previously [1]. From sufficiently concentrated solutions of ferrocenylalcohols in 95% ethanol (5×10^{-3} *M* for the UV-measurements) and in acetone (1×10^{-1} *M* for the measurements in the visible) aliquots of 0.020 to 0.070 ml, depending on the compound, were transferred into the silica cell with an Agla microsyringe and diluted with 3 ml of the sulfuric acid or perchloric acid solvent. These solutions were immediately used for the spectrophotometric measurements, the time interval between the addition of the acid and the spectral recording being about 15 sec.

In sulfuric acid solution all reactions for which the pK_{R^+}'s were determined (vide infra and Table 3) were found to be reversible and the spectral properties of the carbocation-containing solutions were found to be stable over prolonged periods of time at any given acid concentration. In contrast, when the ionization of ferrocenylmethanol and 1-ferrocenylethanol was examined in aqueous perchloric acid under identical conditions the absorption spectra changed with time at all tested acid concentrations, showing an absorbance increase that was especially fast and strong at the intermediate perchloric acid concentrations where the conversion of the alcohol into the carbocation is incomplete. The change is probably due to oxidation to the ferricenium ion as indicated by a comparison with the spectrum of an authentic specimen of an α-hydroxyethylferricenium salt (nitrate) especially in the region of 620 nm where no absorption of the carbocation is present; the comparison is less certain in the 255 nm region where both carbocation and ferricenium ion show absorption bands.

In aqueous sulfuric acid the determination of the equilibrium constants was not praticable for 1′-cyano-, 1′-carboxy and 1′-acetyl-1-α-hydroxyethylferrocenes.

In water, the cyano derivative showed an absorption maximum at 210 nm which rapidly disappeared in acid solution even at low acid concentrations, and no definite carbocation absorption shows up in the vicinity of the 260 nm region at H_2SO_4 concentrations as high as 50%. The cyano group is probably involved in the acid-catalyzed reaction, an analogous behavior being observed for cyanoferrocene in H_2SO_4 solution [24]. The carboxy derivative showed a maximum in water at 280 nm (ε 9200). In the range 8—60% H_2SO_4 a maximum in this region was absent and appeared again in 80% H_2SO_4 at 262 nm (ε 1×10^4). Probably the carboxy group is protonated first and the ionization of the alcohol occurs only at very high acid concentrations.

An intramolecular interaction (hydrogen bond) may be responsible for the observed anomalous behavior. A similar interaction has been investigated in detail elsewhere [11] in the case of the 1′-acetyl derivative.

The evaluation of the equilibrium constants was carried out according to eqn. 1, defining the acidity function J_o where $Q = (A_{R^+} - A)/(A - A_{OH})$ [15] is defined as the concentration ratio of the carbocation to the alcohol. A, A_{R^+}

TABLE 4

TYPICAL DATA FOR THE EVALUATION OF pK_{R^+} OF α-HYDROXYETHYLFERROCENE (c 1.26 × 10^{-4} M) IN AQUEOUS H_2SO_4

% H_2SO_4	A [a]	Log Q	pK_{R^+}
5	0.549	−0.54	−0.61
6	0.603	−0.41	−0.64
8	0.757	−0.11	−0.59
12	0.963	+0.27	−0.69
14	1.077	+0.52	−0.68
15	1.114	+0.62	−0.70
16	1.143	+0.71	−0.73

[a] Absorbance at 258 nm.

and A_{OH} are the measured absorbances at a given wavelenth of the solution under investigation, of the ferrocenyl carbocation and of the alcohol, respectively. The J_o values were as reported in the literature [12]; the pK_{R^+} values were calculated from the above expression for J_o. The pK_{R^+} determinations were carried out at varying wavelengths in the range 255—265 nm and in one case (ferrocenylmethanol), also at 238 nm. Typical data are reported in Table 4 and show the independence of the pK_{R^+} values of the acid concentration.

The following method was also developed for a more convenient determination of the pK_{R^+} values. By plotting log Q as an absolute quantity vs. the J_o values, the experimental points fall along two straight lines (slopes of opposite signs), which were then evaluated by the least-squares method. The abscissa corresponding to the interception of the two lines represents the pK_{R^+} value. This method gave results in very good agreement with those obtained by eqn. 1 and was also applied to the data of triarylcarbinols [12]. The treatment was particularly useful for the determination of the pK_{R^+} value for phenylferrocenylmethanol. Since the solubility of the compound in aqueous solution is extremely low, the spectrophotometric measurements could not be performed in the whole range of acid concentrations. Then it was necessary to record the spectrum of the carbocation at varying high acid concentrations and decrease the acid concentration until the solubility limit was reached. On plotting log Q vs. J_o the pK_{R^+} value was obtained by extrapolation.

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