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ORGANOMETALLIC CHEMISTRY

V*. PROTONATION OF ACYLFERROCENES UNDER STABLE ION CONDITIONS IN FSO_3H–SO_2ClF SOLUTION

GEORGE A. OLAH and Y. K. MO**
Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106 (U.S.A.)

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SUMMARY

Protonation of acylferrocenes (FeCOR) in FSO_3H–$SO_2ClF(SO_2)$ solution was studied by PMR spectroscopy. The site of protonation is found to be at the carbonyl oxygen atom. Temperature dependent PMR spectra of protonated acylferrocenes $FeCROH^+$ ($R = CH_3$, C_2H_5, C_6H_5, OCH_3) were observed indicating intermolecular hydrogen exchange with the acid solvent system. In addition the PMR spectra of acylferrocenes in FSO_3H–$SO_2ClF(SO_2)$ were found to be dependent upon the acid concentration.

INTRODUCTION

Protonation of metallocenes, including ferrocene, in strong acids such as $BF_3 \cdot H_2O$ and CF_3COOH was reported by Curphey, Santer, Rosenblum and Richards[2]. The site of protonation, as revealed by PMR spectroscopy, was found to be at metals. Similar results were reported by Pavlik and co-workers on infrared spectroscopic study of the protonation of ferrocene in strong acids[3]. The Lewis basicity of transition metal complexes is known and has been reviewed by Kotz and Pedrotty recently[4]. A series of α-ferrocenylcarbenium ions*** has been directly observed by PMR spectroscopy. Their behavior has been attributed to the nucleophilic participation of the non-bonding electrons on the iron atom. On the other hand, an infrared investigation of the protonation of acylferrocenes by HCl or DCl (in gas phase) was reported by Rubalcava and Thomson[7]. However, their results were inconclusive since the structure of the ions formed is questionable. Thus, protonation of acylferrocenes in strong acid solution is of particular interest, because the site of protonation and the participation of the metal atom in α-ferrocenylcarbenium ions ($FeCROH^+$) are not yet well understood in these systems.

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* For Part IV see ref. 1.

** Post-doctoral research associate 1972–1973.

*** For a discussion of the general concept of carbocations and differentiation of trivalent carbenium ion from penta- (or tetra-)coordinated carbenium ions, see ref. 5. For a review concerning α-ferrocenylcarbenium ions see ref. 6.

TABLE I

PMR PARAMETERS OF ACYLFERROCENES (FcCOR) AND THEIR PROTONATED SPECIES (FcCRO$^+$H)[a]

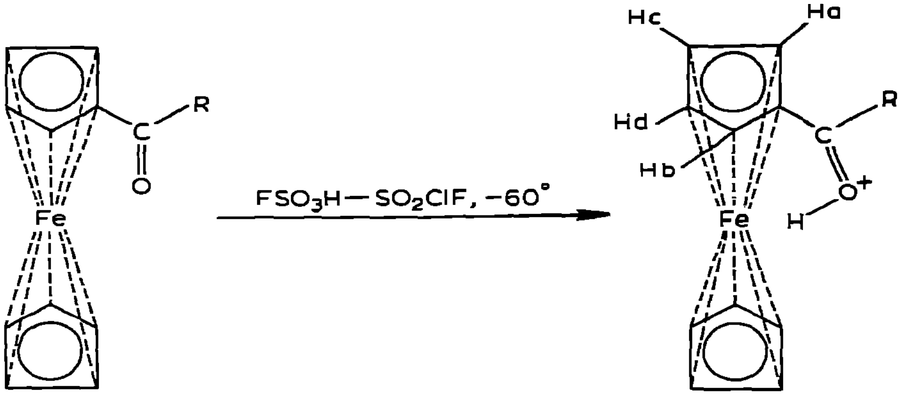
R	*Solvent system, Temp. (°C)*	H_a	H_b	H_c	H_d	*Unsub. ring*	=O^+–H	*R*
Ia R=H	SO_2ClF, −20°	4.86 (t) *J* 1.5	4.86 (t) *J* 1.5	4.71 (t) *J* 1.5	4.71 (t) *J* 1.5	4.37 (s)		9.92 (s)
IIa R=H	FSO_3H–SO_2ClF, −60°	4.67 (d) *J* 2	5.42 (d) *J* 2	6.00 (t) *J* 2	6.35 (t) *J* 2	5.01 (s)	[b]	9.50 (s)
Ib R=CH_3	SO_2ClF, −20°	4.60 (t) *J* 1.5	4.60 (t) *J* 1.5	4.50 (t) *J* 1.5	4.50 (t) *J* 1.5	4.20 (s) *J* 1.5		2.28 (s)
IIb R=CH_3	FSO_3H–SO_2ClF, −101°	5.17 (s(br))	5.42 (s(br))	6.03 (s(br))	6.03 (s(br))	4.75 (s)	11.2 (br)	2.52 (s)
Ic R=C_2H_5	SO_2ClF, −30°	4.84 (s(br))	4.84 (s(br))	4.60 (s(br))	4.60 (s(br))	4.28 (s)		2.82 (q, CH_2) *J* 7, 1.27 (t, CH_3) *J* 7
IIc R=C_2H_5	FSO_3H–SO_2ClF, −90°	5.20	5.50	6.13	6.13	4.90 (s)	11.0 (br)	3.1 ((br), CH_2) 1.6 ((br), CH_3)
Id R=C_6H_5	SO_2, −20°	4.70 (t)	4.70 (t)	4.60 (t)	4.60 (t)	4.07 (s)		7.4 (m) 7.8 (m)
IId R=C_6H_5	FSO_3H–SO_2ClF, −105°	5.1 (s(br))	6.0 (s(br))	6.0 (s(br))	6.3 (s(br))	4.80 (s)	11.3 (br)	8.2 (m)
If R=CH_2Cl	SO_2, −20°	4.6 (m)	4.6 (m)	4.5 (m)	4.5 (m)	4.16 (s)		4.37 (s)
IIf R=CH_2Cl	FSO_3H–SO_2 −60°	5.1 (s(br))	5.6 (s(br))	6.28 (t) *J* 3	6.50 (t) *J* 3	5.10 (s)	[b]	4.90 (d), *J* 16 4.50 (d), *J* 16
Ie R=OCH_3	SO_2, −20°	4.94 (t) *J* 2	4.94 (t) *J* 2	4.53 (t) *J* 2	4.53 (t) *J* 2	4.30 (s)		3.93 (s)
IIe R=OCH_3	FSO_3H–SO_2 −106°	5.3 (s(br))	5.3 (s(br))	5.3 (s(br))	5.6 (s(br))	4.66 (s)	13.0 (br)	4.40 (s)

[a] Proton shifts are referred to external capillary TMS.

[b] =O$^+$–H proton is not observable.

RESULTS AND DISCUSSION

We presently wish to report our results of protonation of a series of acylferrocenes (FeCOR, R = H, CH_3, C_2H_5, C_6H_5, OCH_3 and CH_2Cl, Ia–If) in FSO_3H–$SO_2ClF(SO_2)$ at low temperature. The PMR parameters of the six protonated acylferrocenes ($FeCROH^+$) and their precursors (FeCOR, Ia–If) are summarized in Table 1.



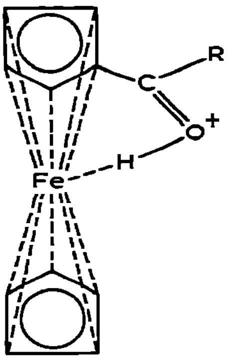
(Ia) R = H
(Ib) $R = CH_3$
(Ic) $R = C_2H_5$
(Id) $R = C_6H_5$
(Ie) $R = OCH_3$
(If) $R = CH_2Cl$

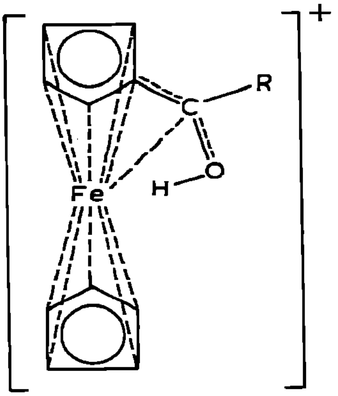
(IIa) R = H
(IIb) $R = CH_3$
(IIc) $R = C_2H_5$
(IId) $R = C_6H_5$
(IIe) $R = OCH_3$
(IIf) $R = CH_2Cl$

Attempted protonation of acylferrocenes in FSO_3H–SbF_5–SO_2ClF solution generally gave only tar or unidentified solid materials, presumably due to oxidative side reactions of the sensitive ferrocene system by antimony pentafluoride. In FSO_3H–$SO_2ClF(SO_2)$, however, clear solutions were obtained and the site of protonation was found at the carbonyl oxygen atom (not at the iron atom) as the $=O^+H$ proton generally shows a PMR absorption more deshielded than δ 10.0. Protons attached to a metal (as in protonated ferrocene[2]) are highly shielded. For example, protonated ferrocene shows an Fe–H PMR absorption[2] at δ -2.03. In protonated acylferrocenes IIa–IIf, the lone-pair of the iron atom can stabilize the ions by hydrogen bonding (III)[4] and also by charge delocalization (IV) as in α-ferrocenylcarbenium ions[6].

The unusual stability of protonated acylferrocenes ($FeCROH^+$) is reflected by the fact that some acylferrocenes (III, $R = CH_3$, C_2H_5, C_6H_5 and OCH_3) can be protonated in FSO_3H–$SO_2ClF(SO_2)$ solution to form the static non-exchangers at low temperatures, while aliphatic aldehydes and ketones do not. On the other hand, they behave similarly to aromatic aldehydes and ketones in the same acid solvent system.

The PMR spectrum of protonated formylferrocene (IIa) in excess FSO_3H–$SO_2ClF(SO_2)$ solution (Fig. 1) shows a sharp singlet at δ 5.01 (5H) for the unsubstituted ring protons, two doublets at δ 4.67 (H_a, J 2 Hz), and 5.42 (H_b, J 2 Hz) and two triplets at δ 6.00 (H_c, J 2 Hz) and 6.35 (H_d, J 2 Hz) for the substituted ring protons.





(III) (IV)

R=H, CH_3, C_2H_5, C_6H_5, OCH_3, CH_2Cl

The assignment of these protons is based on comparison with the reported PMR data of α-ferrocenylcarbenium ions[7]. Our results show that the substituted ferrocenyl ring as well as the $C_{Fe}=C_{\alpha}$ partial double bond are rigid. The H_a and H_b protons closer to the protonated carbonyl group ($C=O^+-H$) are less deshielded than the H_c and H_d protons, presumably due to the partial charge delocalization into the ring (resonance effect). Furthermore, due to the anisotropy effect of the protonated carbonyl

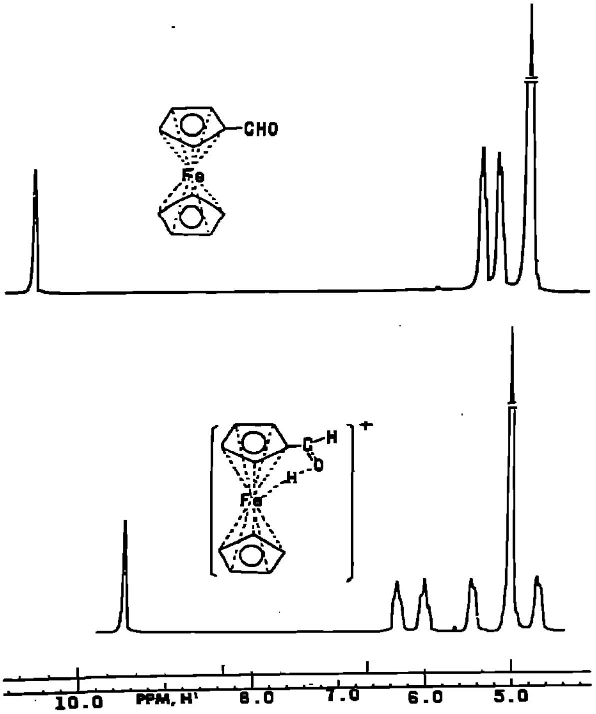


Fig. 1. PMR spectra of formylferrocene (upper trace) and its protonated species (lower trace).

group, H_b and H_d protons are more deshielded than H_a and H_c protons, respectively. The OH proton was not observable (in the range −90° to −10°), presumably due to rapid hydrogen exchange with the acid solvent system. In order to slow down the exchange process, we attempted to protonate Ia in $FSO_3H–SbF_5–SO_2ClF$ solution. Due to obvious oxidative side reactions the solution became viscous and the PMR absorption lines were too broad to be interpreted. The PMR of IIa in excess $FSO_3H–SO_2ClF(SO_2)$ is temperature independent ranging from −90 to −10°.

Protonation of acetylferrocene (Ib) and propionylferrocene (Ic) takes place similarly in excess $FSO_3H–SO_2ClF(SO_2)$. The PMR spectrum of protonated acetylferrocene is temperature dependent and is shown in Fig. 2. At −101°, the "frozen-out" protonated acetylferrocene IIb was observed, the OH proton showing a broadened singlet at δ 11.2. The OH-resonance becomes very broad at −90° and merges with the acid peak at higher temperatures (> −80°). The unsubstituted ring protons and the CH_3CO protons display two singlets at δ 4.75 and 2.28, respectively. They are slightly deshielded when compared with the parent compound, indicating the inductive effect upon protonation of Ib (Table 1). Due to the anisotropy effect of the carbonyl group, we assign the H_a proton to the broadened one-proton singlet at δ 5.17 and the H_b proton to the other more deshielded broadened singlet at δ 5.42. Such effect diminishes in the H_d proton as both H_c and H_d protons display a broadened two-proton singlet at δ 6.03.

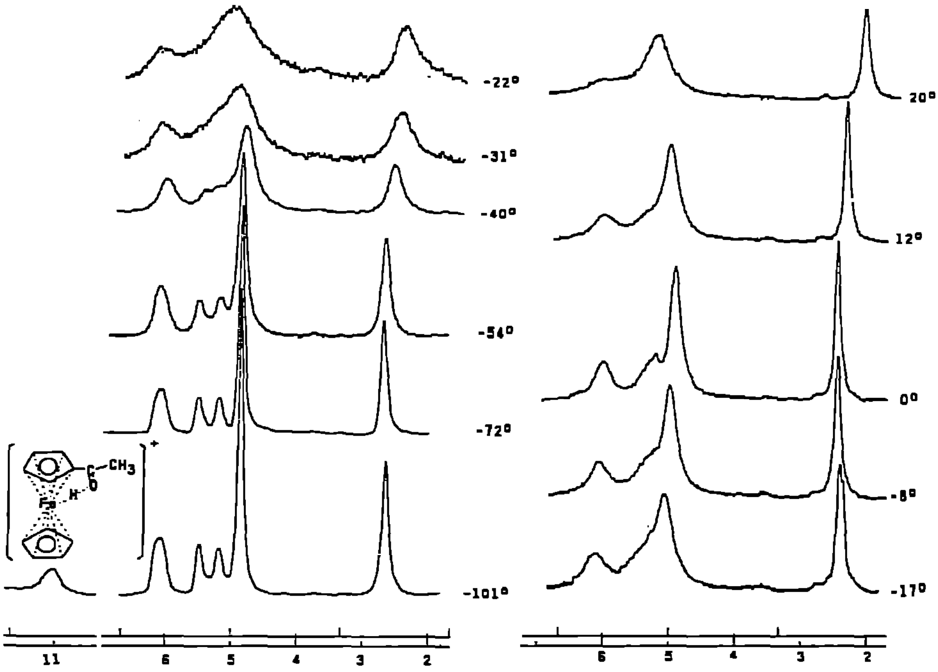


Fig. 2. Temperature dependent PMR spectra of protonated acetylferrocene in $FSO_3H–SO_2ClF$ (left) and in neat FSO_3H (right).

The temperature dependent PMR spectra of protonated acetylferrocene in FSO_3H–$SO_2ClF(SO_2)$ solution (Fig. 2, left) and in neat FSO_3H (Fig. 2, right) are interesting. Due to the relatively low boiling point of SO_2ClF, protonation of Ib in neat FSO_3H was chosen for the −22 to 20° temperature range. This solution became very viscous at lower temperature (ca. −30°). However, the PMR spectra of IIb in FSO_3H and in FSO_3H–$SO_2ClF(SO_2)$ are identical at −22°. It was thus possible to study the temperature dependent PMR spectra of IIb in the two media from −101 to 20°. Above 20°, acetylferrocene decomposes to yet unidentified products in neat FSO_3H solution.

The CH_3CO proton absorption of protonated acetylferrocene IIb gradually becomes more shielded from −101° (at δ 2.52) to −20° (at δ 2.18). In sharp contrast, the unsubstituted ring proton absorption is broadened and gradually becomes deshielded from −101° (at δ 4.75) to 20° (at δ 5.24). These data indicate that deprotonation of the protonated carbonyl oxygen atom takes place with increasing temperature, and, at the same time, C-protonation of the unsubstituted ring does occur. The two broadened absorptions of protons H_a and H_b also collapse to a broadened peak at 0°, indicating the C_{Fe}=C_α bond is freely rotating at this temperature. Thus, these data indicate that protonated acetylferrocene IIb undergoes hydrogen exchange with the acid solvent system at higher temperature.

$$\underset{(Ib)}{FeCOR} + H^+ \rightleftharpoons \underset{(IIb)}{FeCROH^+}$$

Protonation of propionylferrocene Ic in FSO_3H–$SO_2ClF(SO_2)$ also gave the corresponding carbonyl-protonated species IIc. The PMR data of IIc are tabulated in Table 1. Temperature dependent PMR spectra of IIc were also observed and showed close similarity to those of IIb.

Benzoylferrocene (Id) was protonated in FSO_3H–SO_2ClF solution at low temperature to give ion IId. The "frozen-out" ion IId could only be observed at −105°, the OH proton showing a broadened singlet absorption at δ 11.3 (Fig. 3, bottom trace). It is of interest to note that the four protons of the substituted ring display only three slightly broadened singlets at δ 5.1, 6.0 and 6.3 (1/2/1). The most deshielded absorption can be assigned to proton H_d and the most shielded absorption to proton H_a. Protons H_b and H_c are assigned to the two-proton absorption at δ 6.0. The deshielding effect of proton H_b could be caused by the anisotropy effect of the phenyl ring. The aromatic protons show a broadened multiplet centered at δ 8.2. The aromatic proton absorption is much different from that of protonated acetophenone in FSO_3H–SO_2ClF at −100°. In protonated acetophenone, the aromatic proton absorptions are well separated in the deshielding order *ortho* > *para* > *meta*. These data indicate IId has lesser charge delocalization into the phenyl ring than protonated acetophenone.

Temperature dependent PMR spectra of IId were also observed (Fig. 3). As the temperature increased from −105 to −84°, the OH absorption disappeared. At the same time, all other PMR absorptions became slightly broadened, and they became very broad at −63°. Further raising of the temperature (ca. −21°) caused the ferrocenyl protons of both rings to collapse to a very broad peak at δ 5.1. This could be due to ferrocenyl ring C-protonation taking place at this temperature (or IId may undergo hydrogen exchange with the solvent system). The broadening and deshielding

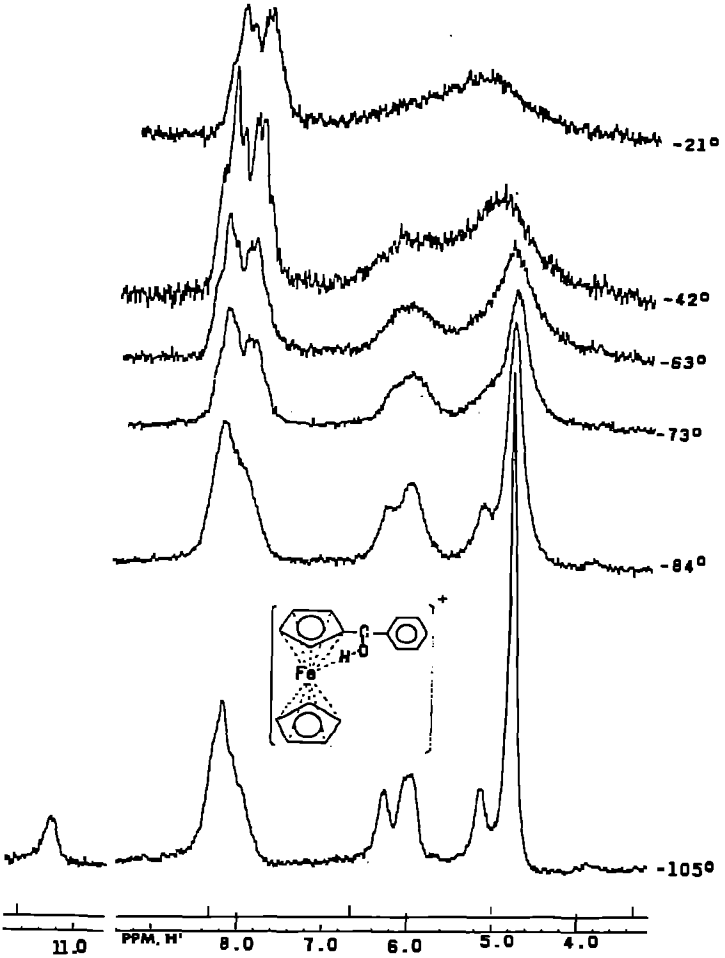


Fig. 3. Temperature dependent PMR spectra of protonated benzoylferrocene in FSO_3H-SO_2ClF.

of the unsubstituted ferrocenyl ring proton absorption as the temperature increased suggests ring C-protonation. Furthermore, the aromatic proton absorption of IId in FSO_3H-SO_2ClF at −21° remains similar to its precursor (Id) in SO_2ClF.

Methyl ferrocenoate (Ie) was also protonated in $FSO_3H-SO_2ClF(SO_2)$ solution at −106° to give ion IIe. The PMR spectrum of ion IIe is shown in Fig. 4 (bottom trace). The OH proton shows a very broad PMR absorption at δ 13.0 indicating slow hydrogen exchange with the solvent system. The methoxy and the unsubstituted ring protons show two singlets at δ 4.40 and 4.66, respectively. There are only two broadened singlet absorptions at δ 5.3 and 5.6 in a ratio of 3/1 for the four protons in the substituted ferrocenyl ring. Due to the similar anisotropy effect of the two carbonyl groups in ion IIe, protons H_a and H_b display the same PMR absorption at δ 5.3 (broadened singlet). Proton H_c also shows a coincidental PMR absorption at δ 5.3. The most deshielded, broadened singlet at δ 5.6 is assigned to proton H_d. The PMR spectrum of ion IIe is again temperature dependent (Fig. 4). The methoxy PMR

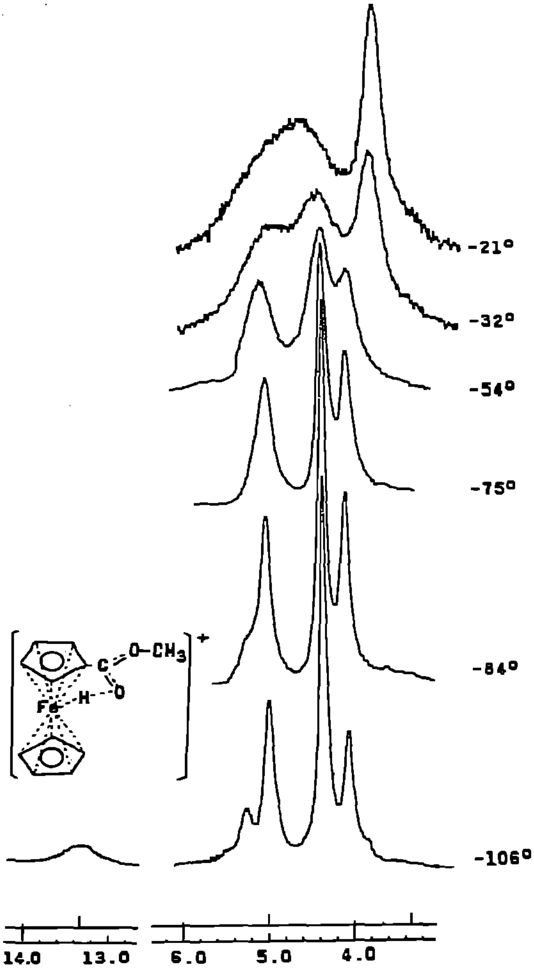


Fig. 4. Temperature dependent PMR spectra of protonated methyl ferrocenate in FSO_3H-SO_2ClF.

singlet absorption becomes broadened and shielded at higher temperature indicating a protonation–deprotonation process (hydrogen exchange with the solvent system). The unsubstituted ring proton absorption is, however deshielded and also broadened at higher temperatures. The two PMR absorptions of the substituted ring protons collapsed at −75° and finally merged with the unsubstituted ring proton absorption to give a single broadened peak (centered at δ 4.90) at −21°. These data suggest that protonation–deprotonation processes occur at the carbonyl oxygen as well as at the unsubstituted ring.

Protonation of chloroacetylferrocene (If) in $FSO_3H-SO_2ClF(SO_2)$ solution was also studied. The PMR spectrum of the resulting solution shows two sets of doublets (AB quartet) at δ 4.50 and 4.90 for the methylene protons. The methylene protons are non-equivalent and couple to each other with a geminal coupling constant of 16 Hz[8]. These data show the rigidity of the methylene group in IIf. In contrast, the methylene protons of its parent (If) show a singlet at δ 4.37. The unsubstituted ferrocenyl ring protons display a singlet at δ 5.10 (0.94 ppm deshielded from its parent). There are three one-proton PMR absorptions at δ 5.6 (broadened singlet); 6.28 (triplet, J 3 Hz) and 6.50 (triplet, J 3 Hz) which are assigned to the substituted ferrocenyl ring protons (H_b, H_c and H_d, respectively). Proton H_a shows a coincident PMR absorption with the unsubstituted ring absorption at δ 5.1. The OH proton was not observed even at the lowest accessible temperature (ca. −96°), probably due to the rapid hydrogen exchange with the solvent system. Furthermore, the PMR spectrum of IIf is temperature independent in the range from −96 to −10°. This behavior of chloroacetylferrocene in FSO_3H–$SO_2ClF(SO_2)$ solution is similar to that of formylferrocene (Ia).

Dependence of PMR spectra on acid concentration. The PMR spectra of acylferrocenes in FSO_3H–$SO_2ClF(SO_2)$ solution was found to be dependent on acid concentration. For example, the PMR spectrum of formylferrocene in SO_2ClF at −20° shows a singlet at δ 4.37 (5 H) for the unsubstituted ring protons and two triplets at δ 4.71 (2 H) and 4.86 (2 H) for the substituted ring protons. The more deshielded triplet is assigned to the protons H_a and H_b and the shielded triplet to the protons H_c and H_d (relative to the formyl group)[9]. When 10 mol % of FSO_3H was added to the above solution, each of the PMR absorption lines was slightly deshielded, and a very deshielded OH absorption was found at δ 13.8. When 20 mol % of FSO_3H was added, the four substituted ring protons became accidentally equivalent and display a sharp singlet at δ 4.90. The OH absorption was slightly further shielded to δ 13.4. The unsubstituted ring proton absorption is a singlet at δ 4.43. The PMR spectra of the above solutions were found temperature independent in the range from −90 to −10°. From the results it may be interpreted that an intermolecular proton exchange between formylferrocene and protonated formylferrocene takes place

$$^{*}FeCHO + FeCHOH^{+} \rightleftharpoons {}^{*}FeCHOH^{+} + FeCHO$$

When the concentration of FSO_3H was increased to 50 mol %, the sharp singlet for the four equivalent substituted ring protons split into two PMR absorptions at δ 5.00 and 5.31. The unsubstituted ring protons showed again a singlet at δ 4.63. The OH proton displayed a slightly broadened singlet at δ 14.4. The two PMR absorptions of the four substituted ring protons are further split into four one-proton absorptions at δ 4.78, 5.41, 5.81 and 6.20 when equimolar FSO_3H was used to protonate formylferrocene in SO_2ClF at −60°. The OH proton displayed a slightly broadened singlet at δ 14.1. Indeed, the PMR spectrum of this solution is similar to that of formylferrocene in excess FSO_3H–$SO_2ClF(SO_2)$ solution, except that each PMR absorption is slightly deshielded in the latter (Table 1). The study of acid concentration dependent PMR spectra of acylferrocenes in FSO_3H–$SO_2ClF(SO_2)$ solution further suggests the previously discussed PMR assignment of ion IIa.

Acid concentration dependent PMR spectra of other acylferrocenes (Ib–If) were also observed. The results are again in accord with the PMR assignments of protonated acylferrocenes (IIb–IIf), *i.e.*, protons H_a and H_b of all the six acylferrocenes (Ia–If) studied are more deshielded than protons H_c and H_d, while in their protonated derivatives the deshieldings are reversed.

CONCLUSIONS

The site of protonation of acylferrocenes in FSO_3H–$SO_2ClF(SO_2)$ solution was found to be at the carbonyl oxygen atom. The stability of the ions formed is related to the nature of the acyl group. The "frozen-out" ions can be observed only when the substituents (R) of the acyl group are capable of stabilizing the ions formed (as in case of IIb–IIe). In addition, these "frozen-out" ions can be only observed at very low temperature ($< -90°$) and their PMR spectra are temperature dependent (Figs. 2–4).

Protonation of the iron atom in acylferrocenes was not observed, although the proton attached to the carbonyl oxygen (in ions IIa–IIf) could, at the same time, be associated (via hydrogen bonding) with the iron atom. Protonation of ferrocene itself in FSO_3H–$SO_2ClF(SO_2)$ solution at $-80°$ also shows no evidence of Fe-protonation. However, the PMR spectrum of the solution shows a deshielded (0.9 ppm from ferrocene in $SO_2ClF(SO_2)$) singlet absorption at δ 5.00, indicating hydrogen exchange with the acid solvent system. On the other hand, from the temperature dependent study of ions IIb–IIe, the deshielding of the substituted ring protons at higher temperature suggest that ring protonation may occur under these conditions. Obviously C-protonation is a higher energy process than n-protonation in these systems*. We were, however, unable to observe the static C-protonated forms of acylferrocenes under the experimental conditions. Data concerning the protonation of acylferrocenes in FSO_3H–$SO_2ClF(SO_2)$ solution under stable ion conditions give useful information related to the electrophilic reactivity of these compounds.

EXPERIMENTAL

Materials

All acylferrocenes used were commercially available materials (Aldrich Chemical Company, Research Organic/Inorganic Chem. Corp. or Wind River Chemicals). Fluorosulfuric acid (Allied Chemical Co.) was twice distilled before use.

NMR Spectra

A Varian Associate Model A56/60A NMR spectrometer equipped with a variable temperature probe was used to obtain the PMR spectra. Proton chemical shifts are referred to external (capillary) TMS.

Preparation of the ions

Samples of protonated acylferrocenes were prepared by dissolving approximately 0.2 g of acylferrocenes to 1.5 ml of fluorosulfuric acid–sulfuryl chloride fluoride solution at $-78°$. The reaction mixture was vigorously stirred until a clear homogeneous solution was obtained and was then transferred to an NMR tube for spectral studies.

Quenching of FSO_3H–SO_2ClF solutions of protonated acylferrocenes with ice-water regenerated the starting acylferrocenes, showing that no protolytic cleavage reactions took place under the experimental conditions.

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* n-Protonation of phenol and anisole was observed only at low temperature (ca. $-105°$) while C-protonation was found at higher temperature ($-60°$) see ref. 10.

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