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STABLE CARBOCATIONS

XI *. H/D EXCHANGE REACTIONS OF FERROCENYLALKYLIUM IONS IN CF_3CO_2D SOLUTION

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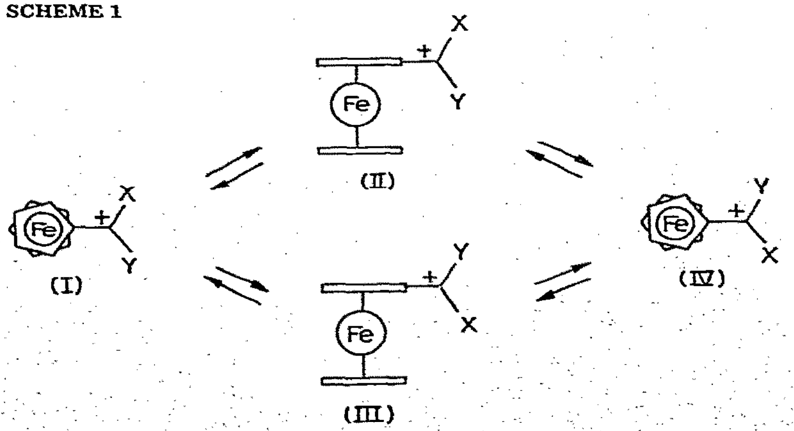
Summary

In CF_3CO_2D solution, tertiary 1-ferrocenylalkylium ions undergo slow H/D exchange of protons attached to the carbon atoms bonded to the carbenium atom. Evidence has been obtained that this isotope exchange is facilitated by intramolecular proton transfer to the iron atom.

Introduction

In an earlier paper [2], we reported a ^1H NMR study of the magnitude of the energy barrier to rotation around the exocyclic bond ($Fc—C^+$) in 1-ferrocenylalkylium ions dissolved in a strong protic acid. During this investigation, it was necessary to exclude the possibility that interconversion of the ground-

SCHEME 1



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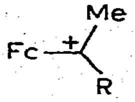
* For part X see ref. 1.

state conformations I and IV occurs by cation deprotonation to give a 1-ferrocenylalkene followed by fast rotation and reprotonation. Such a mechanism was eliminated since negligible incorporation of deuterium by the cation was detected during the period of torsional isomerisation when CF_3CO_2D was used as solvent.

We have since discovered, however, that slow H/D exchange of protons attached to the carbon atoms adjacent to the formal C^+ centre does occur when cations of this type are maintained for longer periods in CF_3CO_2D solution and we describe herein a study of this reaction.

Results and discussion

A series of 1-ferrocenyl-1-methylalkylium ions (Va—Vh) was prepared by dissolving the corresponding alcohols, FcCR(OH)Me, in CF_3CO_2D. The ^1H NMR spectra of these freshly prepared solutions were indistinguishable from those obtained for CF_3CO_2H solutions of the same alcohols. These spectra, which are summarised in Table 1, each contained two sharp singlet resonances characteristic of the C_5H_5 and Me groups (around τ 5.0 and 7.7 respectively). When these solutions were stored at 33°C for prolonged periods, changes in their spectra became evident. Although the ferrocenyl proton signals remained unaltered with barely perceptible loss of definition, the $Me—C^+$ singlet slowly collapsed and finally disappeared indicating H/D exchange of the associated protons. Likewise, slow disappearance of the signals attributable to the $CH_2—C^+$ protons of the R group of the cations (Vb, Ve) was observed. Exchange of the $CH—C^+$ proton of the i-Pr group of the cation Vc was also clearly indicated by the gradual replacement of the two i-Pr methyl doublets in the original spectrum by two singlets centred on the doublets[*] ($CHMe_2 \rightarrow CDMe_2$).



(V)

(a) R = Me ; (b) R = Et ; (c) R = i-Pr ;
(d) R = t-Bu ; (e) R = CH_2Ph ; (f) R = Ph ;
(g) R = *m*-tolyl ; (h) R = *p*-tolyl ; (i) R = H

In the spectrum of the cation Vd, slow H/D exchange of the t-Bu protons was noted. However, we have previously shown [4] that, in CF_3CO_2H solution, ferrocenylalkylium ions may undergo a double-shift rearrangement which in this case would cause scrambling of the four Me groups (FcC^+MeCMe_3) of the ion with attendant incorporation of deuterium by the t-Bu group. With all of the other cations investigated, isotope exchange was found only for those protons attached to the carbon atoms neighbouring the carbenium atom C(α). The instability of CF_3CO_2D solutions of the secondary cation Vi, which decomposes to paramagnetic species, prevented spectroscopic study of H/D exchange.

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[*] The i-Pr methyl groups of the cation Vc are anisochronous (cf. [3]).

TABLE 1

^{1}H NMR SPECTRA OF FERROCENYLALKYLIUM IONS V [a]

Cation	Ferrocenyl protons (τ, ppm) [b]			Other protons (τ, ppm)	
	H(2,5)	H(3,4)	H(1′—5′) [c]	Me [c]	R
Va	5.05 (t)	3.72 (t)	5.14	7.77	7.77 (s)
Vb	5.05—5.2	3.66 (t)	5.10	7.74	7.25—7.7 (CH_2)
					8.65 (t, Me)
Vc	4.85—5.0	3.55—3.7	5.02	7.90	7.13 (sp, CH)
					8.42, 8.66 (2d, Me_2)
Vd	4.55—4.75	3.4 —3.75	5.01	7.99	8.49 (s)
Ve	4.8 —5.1	3.62 (t)	5.05	7.87	2.55—2.8 (Ph)
					6.24 (s, CH_2)
Vf	4.5 —4.7	3.4 —3.7	5.12	7.53	2.0 —2.5
	4.9 —5.1				
Vg	4.6 —4.75	3.45—3.75	5.16	7.58	2.3 —2.6 (C_6H_4)
	4.95—5.1				7.50 (s, Me)
Vh	4.55—4.7	3.45—3.75	5.17	7.60	2.1—2.65 (C_6H_4)
	4.9 —5.05				7.60 (s, Me)
Vi	4.85—5.05	3.55—3.75	4.97	7.75 (d)	2.88 (q)
	5.45—5.6	3.75—3.9			
RcC^+Me_2	4.62 (t)	3.82 (t)	4.74	7.72	—

[a] For freshly prepared CF_3CO_2D solutions with Me_4Si as internal reference; multiplets unless indicated otherwise; (s) singlet, (d) doublet, (t) triplet, (q) quartet, (sp) septet; identical spectra were obtained for CF_3CO_2H solutions of the same alcohols. [b] The location of the ring protons relative to the $Me(R)C^+$ substituent is given. [c] Singlet resonance unless indicated otherwise.

When CF_3CO_2D solutions of the cations (Vb—Vh) following isotope exchange were quenched with an excess of Na_2CO_3(aq), loss of D^+ occurred giving alkenylferrocenes as the predominant products. Comparison of the ^{1}H NMR spectra of these alkenes with those of their all-proton analogues confirmed that deuterium incorporation had occurred at those sites indicated by the spectra of the cation precursors, e.g. Vb → $FcC(CD_3){=}CDMe$. With those cations for which, in principle, deprotonation could afford two isomeric alkenes, apparently* exclusive formation of the Saytzeff product was found (^{1}H NMR) in each case; i.e. Vb → $FcCMe{=}CHMe$, Vc → $FcCMe{=}CMe_2$, and Ve → $FcCMe{=}CHPh$. A complex mixture of dimeric products results when acidic solutions of the cation Va are quenched with base [5].

The rates of H/D exchange of the Me protons of the cations (Va—Vh) varied markedly through the series**. The times ($t_{1/2}$) for 50% exchange, given in Table 2, were determined by monitoring changes with time in the relative integrated intensities of the C_5H_5 singlet and the collapsing Me signal in the ^{1}H NMR spectra of equimolar CF_3CO_2D solutions maintained at 33°C and/or 50°C. Comparison of these $t_{1/2}$ values shows that the Me exchange rate increases sharply through the series: (V) R = Me < Ph < Et < CH_2Ph < i-Pr < t-Bu, and R =

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* The presence of more than ca. 5% of the anti-Saytzeff alkenes, whose spectra were available for comparison, would have been detectable from the ^{1}H NMR spectra of the alkene products of quenching.

** For selected substrates, plots of $\log(A_t)$ vs. t (where A_t = relative integrated intensity at time t of the collapsing Me signal in the cation spectrum) showed deviation from a linear relationship. This suggests the operation of a secondary D-isotope effect in the deprotonation of $FcC^+R(CH_3)$, $FcC^+R(CH_2D)$, and $FcC^+R(CHD_2)$.

TABLE 2

TIMES ($t_{1/2}$) FOR 50% H/D EXCHANGE OF Me—C$^+$ AND CH$_2$—C$^+$ GROUPS OF CATIONS V AND X [a]

Cation	$t_{1/2}$ Values (h) [b]			
	Me—C$^+$ protons		CH$_2$—C$^+$ protons	
	33°C	50°C	33°C	50°C
Va	6.5	1.65	—	—
Vb	4.9		2.0	
Vc	1.7		—	—
Vd [c]	0.47		—	—
Ve	2.9		0.58	
Vf	5.4	1.33	—	—
Vg		0.92	—	—
Vh		1.03	—	—
Xa	80		*d*	
Xb	92.		—	—
Xc	*d*	*d*	*d*	*d*
Xd	3.8		*d*	
RcC$^+$Me$_2$	*d*	160.	—	—

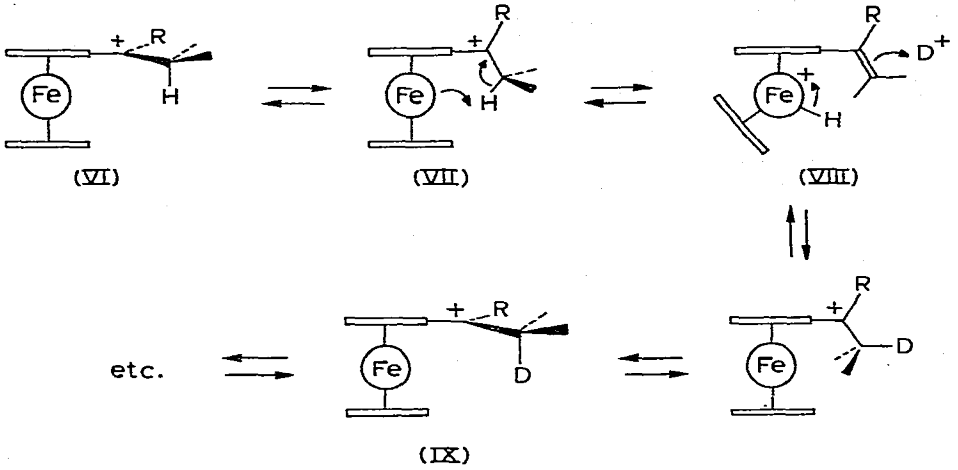
[a] For CF$_3$CO$_2$D solutions. [b] Estimated by monitoring changes in the integrated intensities of the collapsing Me—C$^+$ and CH$_2$—C$^+$ signals in the ^{1}H NMR spectra relative to those of the C$_5$H$_5$ singlet for the cations V and RcC$^+$Me$_2$, the Me$_2$C singlets for the cation Xb, and suitable ferrocenyl proton resonances for the cations Xa, Xc, Xd. [c] At 33°C, the $t_{1/2}$ value for H/D exchange of the t-Bu protons was 20 h (see text). [d] Extremely sluggish H/D exchange (50% exchange not achieved).

Ph $<$ *p*-tolyl $\leqslant$ *m*-tolyl. Similarly, the CH$_2$ protons of the Et group of the cation Vb were found to exchange at a rate much slower than that of the CH$_2$ protons of the benzyl group of the cation Ve. For both of these cations Vb, Ve, CH$_2$ exchange occurred faster than Me exchange (noting the statistical factor).

The mechanism of this isotope exchange must involve slow deprotonation of the cation followed by fast deuteronation of the resulting alkenylferrocene. The instantaneous alkene concentration must be relatively minute (below the level of spectroscopic detection) and it is likely that the original and D-exchanged cations would be of near-identical stabilities (assuming negligible D-isotope effects in this connection). The rate at which exchange occurs, therefore, would be controlled by the magnitude of the free-energy barrier to deprotonation of the cation and this would be sensitive to a number of factors. Firstly, the acidity of a C—H bond adjacent to C(α) would be related to the thermodynamic stability of the C(α)—C(β) double bond developing through deprotonation. However, the variation within the Me exchange rates for the series (Va—Vh) is not satisfactorily accommodated by the anticipated differential effects of substituents R upon the stabilities of alkenes of the type FcCR=CH$_2$ (cf. heats of hydrogenation of terminal alkenes [6]). Nevertheless, differential alkene stability is the most likely factor responsible for the faster rate of exchange of the CH$_2$—C$^+$ protons than of the Me—C$^+$ protons of the cations (Vb, Ve).

Secondly, the ease of proton elimination from a β-carbon atom would be directly related to the positive-charge concentration at C(α) at the transition state for deprotonation. In the ground-state conformations (I, IV), charge allocation to C(α) is strongly attenuated by electron donation from the ferrocenyl group [7]. However, since such conjugative interaction is precluded at the halfway stages (II, III) during rotational interconversion of the ground states (see Scheme 1), the concentration of charge at C(α) would increase during torsion and it seems reasonable to suppose that deprotonation would be much more likely to occur when the cation attains a bisected conformation (II or III). Furthermore, for those cations bearing C(α) substituents of disparate steric bulk, it is obvious that rotation of the less bulky substituent past the pendant FeC_5H_5 group would be the energetically favoured pathway (i.e. via II where $X > Y$). It is clear from earlier work [2] that the rate of rotation around the $Fc—C^+$ bond in cations of the type V is much faster than the rate of deprotonation, as judged by the H/D exchange rates.

SCHEME 2



A mechanism which accounts for the experimental results is suggested in Scheme 2. Following rotation of the cation into a bisected conformation (VI → VII), proton transfer from the *endo*-β-carbon atom to the iron atom, acting as an internal base, can be envisaged. Double-bond deuteronation and iron deprotonation (possibly concerted) of the resulting alkenylferrocenonium ion VIII would generate the H/D-exchanged cation IX as shown. The Lewis base property of the iron atom in ferrocene compounds is well documented [8] and, since $p_\pi—p(d)_\pi$ conjugation between C(α) and the ferrocenyl group is reduced during rotation (vide supra), the base strength of the metal atom would reach a maximum as the ion approaches the bisected conformation VII. As indicated previously, an increase in the steric bulk of the C(α) substituent R would lead to a relative increase in the population of the *endo*-methyl conformation (II; $X = R$, $Y = Me$) with a corresponding acceleration of the rate of Me exchange, in accord with the experimental results (see Table 2).

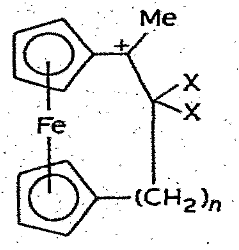
In order to assess the importance or otherwise of iron participation in the H/D exchange process, as indicated in Scheme 2, the behaviour of a series of heteroannularly bridged ferrocenophanyl cations (Xa—Xd) was studied. These cations were prepared in the usual way by dissolution of the corresponding alcohols in CF_3CO_2D and their ^1H NMR spectra are summarised in Table 3. Incorporation of deuterium was investigated as before by monitoring changes with

TABLE 3

^{1}H NMR SPECTRA OF FERROCENOPHANYL CATIONS X^a

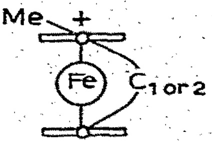
Cation	Ferrocenyl protons (τ, ppm)	Other protons (τ, ppm)		
		Me ^{b}	X_2	$(CH_2)_n$
Xa	3.2 —3.5 (1H), 4.0 —4.25 (3H), 4.65—5.1 (2H), 5.2 —5.45 (2H)	7.19	6.0—6.3	6.4 —7.4
Xb	3.4 —3.6 (1H), 3.9 —4.2 (2H), 4.25—4.45 (1H), 4.9 —5.45 (4H)	7.16	8.21, 8.49 (2s)	6.05, 7.17 (2d)
Xc	3.5 —3.7 (1H), 3.8 —4.0 (1H), 4.8—5.45 (6H)	7.64	7.3—7.5	7.8 —8.5
Xd	3.78 (2H, t), 4.97 (2H, t), 5.21 (3H, d), 5.35—5.5 (1H)	7.69	6.8—7.15	7.25—7.45 (2H) 7.7 —8.25 (4H)

^{a} As for Table 1. ^{b} Singlet resonance.

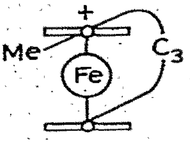


(X)

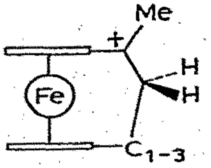
(a) X = H , n = 1 ; (b) X = Me , n = 1 ;
(c) X = H , n = 2 ; (d) X = H , n = 3



(XI)



(XII)



(XIII)

time in the spectra of the cations and by analysis of the spectra of the products formed upon quenching the acidic solutions with base.

As shown by the $t_{1/2}$ values given in Table 2, the Me—C$^+$ protons of the [3]- and [4]-ferrocenophanyl cations (Xa—Xc) undergo exchange at rates very much slower than that of the slowest (Va) of the unbridged analogues. From inspection of molecular models, it is apparent that the interannular 3- and 4-carbon bridging groups of these species are constrained such that the Me groups are restricted to *exo*-environments remote from the iron atom (cf. XI). Metal-assisted deprotonation is thereby prevented and the Me exchange rates are correspondingly depressed. With the [5] ferrocenophanyl analogue (Xd), on the other hand, the increased bridge length permits the ion to adopt a conformation in which metal participation is possible (cf. XII) and the Me exchange occurs at a rate comparable with those of the unbridged cations Vb, Vc. Differences in the relative stabilities of the alkenes resulting from deprotonation of the Me groups of the cations Xa—Xd probably contribute to the variation in the H/D exchange rates but appear unlikely to be solely responsible for the magnitude of the effect observed. For each of the cations Xa, Xc, Xd, exchange of the CH_2—C^+ protons also occurs at an extremely sluggish rate. Although these β-CH_2 groups occupy *endo*-environments adjacent to the iron atom, the conformational constraints imposed upon the interannular bridges prevent intramolecular proton transfer to the metal atom since the C(β)—H bonds are inappropriately oriented (cf. VII and XIII).

Finally, we have investigated the properties of the 1-methyl-1-ruthenocenylethylium ion (RcC^+Me_2). Previous research [2] has established that the free-energy barrier to rotation around the exocyclic bond (Rc—C^+) of a ruthenocenylalkylium ion is appreciably higher than that associated with the corresponding ferrocenyl species. Evidence has also been obtained [8a] that the ruthenium atom in ruthenocenes is a weaker base than the iron atom in ferrocenes. Consequently, if metal-assisted deprotonation (cf. Scheme 2) is an important factor controlling the rate of H/D exchange, it would be expected that ruthenocenylalkylium ions would prove much less reactive in this connection than their ferrocenyl counterparts. In support of this premise, the cation RcC^+Me_2 was found to undergo H/D exchange of the Me protons at a rate very much slower than that of the iron analogue Va (see Table 2).

Experimental

All of the alcohols used in this study have been described previously in the literature. They were prepared from the corresponding ketones by the addition of methyllithium followed by hydrolysis and were purified by thin-layer chromatography on SiO_2. The ^1H NMR spectra of the cations (Tables 1 and 3) were obtained for 0.2 M solutions of the alcohols in CF_3CO_2D using a Perkin—Elmer R12A spectrometer operating at 60 MHz with Me_4Si as internal reference. Isotope exchange was followed by monitoring changes with time in the spectra of solutions thermostatted at 33°C and/or 50°C (see text).

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