Reactions of Ferrocenyl-stabilised Carbocations with Water: Substituent, Medium, Salt, and Solvent Isotope Effects on Rates and Equilibria

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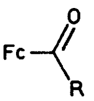
Rates and equilibrium constants have been measured for reactions of ferrocenylalkyl cations $\text{Fc}\overset{+}{\text{C}}(\text{R})\text{Ar}$, $\text{Fc}\overset{+}{\text{C}}\text{Ar}_2$, and $\text{Fc}\overset{+}{\text{C}}\text{H}(\text{CH}{=}\text{CH})_n\text{Fc}$ (R = H, Bu^t, and 1-adamantyl; Ar = Ph and *p*-methoxyphenyl; *n* = 0 and 1) with water in H_2O and in H_2O–MeCN in the absence and presence of mineral acid (HCl or H_2SO_4), and a H_R^{Fc} acidity function has been constructed for reactions in H_2O–MeCN (H_2SO_4). The rates of water addition to the cations and of acid-promoted heterolysis of ferrocenylalkanols are sensitive to structural, steric, and conformational effects. Medium, salt, and solvent isotope effects on rates and equilibria are consistent with a carbocation-like transition state.

THE addition of a nucleophile to a trivalent carbocation in solution is one of the simplest of organic reactions, and structure–reactivity relationships have been investigated extensively. Much of the quantitative work [1-5] has been concerned with studies of the rates of nucleophilic additions to the readily available triarylmethyl cations (*e.g.* tris-*p*-methoxyphenylmethyl and the dye cations Malachite Green and Crystal Violet). Although rates have been measured for reactions of some other systems [1a,c,6] (*e.g.* tropylium and arenediazonium cations), the development of understanding of carbocation reactivity in solution has been hampered by the small number of structural types amenable to kinetic study.

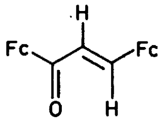
With this problem in mind, we have investigated the rates of nucleophilic addition reactions of transition metal-stabilised carbocations which can be obtained in a wide variety of structural types and which are often isolable in stable salts.[7] By using ferrocenylalkyl cations,[7b] for example, nucleophilic attack at primary, secondary, and tertiary centres can be examined. In this paper, we report a study of equilibria between ferrocenylalkyl cations and related alcohols in aqueous acidic media and of the rates of the forward and reverse reactions. Preliminary accounts of some results have been published.[8]

$\text{p}K_{\text{R}^+}$ *Measurements.*—Problems arise in the determination of $\text{p}K_{\text{R}^+}$ values for equilibria of ferrocenyl-alkanols (4) and -alkyl cations (5) in aqueous acidic media,[9] *viz.* the low solubility in water of most of the alcohols, the fragmentation of some cations in acidic solutions,[10] one-electron transfer reactions of the cations,[11] competing addition–deprotonation reactions of alkyl-substituted carbocations,[8c] and the attendant complication in such cases of cation + alkene coupling reactions.[8a,12] Furthermore, plots of $\log([\text{R}^+]/[\text{ROH}])$ for ferrocenyl substrates in aqueous H_2SO_4 against the Deno H_R acidity function [13] (based on the properties of triarylmethyl indicators) often deviate markedly from unit slope,[9a,d] showing that there are significant differences in activity coefficient behaviour ($\gamma_{\text{R}^+}/\gamma_{\text{ROH}}$) for the two carbocation classes.

Because of the solubility problem, we mostly used H_2O–MeCN (1 : 1 w/w) as solvent for equilibrium and rate studies, and a H_R^{Fc} acidity function was set up for H_2SO_4 in this solvent using (4a)—(5a) and (4b)—(5b) as reference indicators. These cations (5a and b) are stable in solution and the alcohols (4a and b) are


(1)

a; R = Ph
b; R = An
c; R = Bu^t
d; R = Ad
e; R = Fc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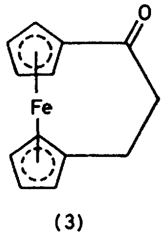
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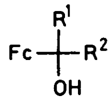
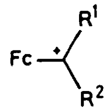
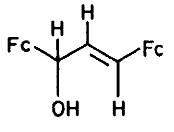

(4)


(5)

a; R^1 = H, R^2 = Ph
b; R^1 = H, R^2 = An
c; R^1 = R^2 = Ph
d; R^1 = Ph, R^2 = An
e; R^1 = R^2 = An
f; R^1 = Ph, R^2 = Bu^t
g; R^1 = An, R^2 = Bu^t
h; R^1 = Ph, R^2 = Ad
i; R^1 = An, R^2 = Ad
j; R^1 = H, R^2 = Fc
k; R^1 = R^2 = H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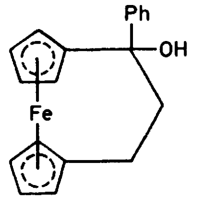
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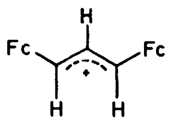
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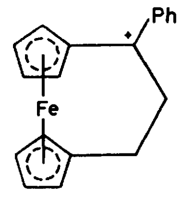
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Fc = ferrocenyl; An = *p*-MeOC_6H_4; Ad = 1-adamantyl sufficiently soluble in water to permit spectroscopic determination of $[R^+]/[ROH]$ equilibrium ratios in aqueous HCl (the alcohols are completely converted into the cations in concentrated aqueous HCl). For both systems, plots of $\log([R^+]/[ROH])$ against $-\log[HCl]$ were linear and of unit slope through the acid concentration range 0.005—0.100M. The corresponding pK_{R^+} values were then obtained conventionally from the $-\log[HCl]$ value at the intercept $\log([R^+]/[ROH]) = 0$. The corresponding plots for equilibria in aqueous H_2SO_4 deviated from unit slope since dissociation of HSO_4^- becomes significant in dilute aqueous solutions.

The $[R^+]/[ROH]$ equilibrium ratios for the two indicators were then redetermined in H_2O–MeCN (1 : 1 w/w) containing H_2SO_4, and H_R^{Fc} values were calculated from these ratios and from the pK_{R^+} values determined previously in water [equation (1)]. Good agreement

$$H_R^{Fc} = pK_{R^+} - \log([R^+]/[ROH]) \qquad (1)$$

(within 0.1 log unit) was found between H_R^{Fc} values calculated for particular H_2SO_4 concentrations using the different indicators. This H_R^{Fc} function thus relates $[R^+]/[ROH]$ ratios for equilibria in H_2O–MeCN (H_2SO_4) to pK_{R^+} values for water as the standard state. The linear $\log([R^+]/[ROH])$ *versus* $-\log[\text{acid}]$ plots for each indicator in H_2O (HCl) and in H_2O–MeCN (H_2SO_4) were parallel and showed that the pK_{R^+} values for the mixed solvent are *ca.* 0.9 log units more negative than those for water. Comparison of plots for the indicators in H_2O (H_2SO_4) and in H_2O–MeCN (H_2SO_4) also showed that HSO_4^- dissociation is decreased in the mixed solvent.

For the tertiary carbocations (5c—i), $[R^+]/[ROH]$ equilibrium ratios were determined spectroscopically for solutions in H_2O–MeCN containing H_2SO_4 at molarities appropriate for each system and chosen to cover a range of indicator ratios from 0.1 to 10. As noted earlier,[9a,10] these tertiary carbocations are unstable in aqueous acidic solutions and decompose with liberation of the pentafulvene ligand. However, equilibration between cation and alcohol occurs much faster than fragmentation,[14] and the equilibrium ratios could be calculated by extrapolation of the absorbance values back to the time of mixing. This procedure is reasonably satisfactory for the cations (5c—e), but it is less so for (5f—i) where much more concentrated acid was required and where fragmentation is therefore much more rapid.[14] The pK_{R^+} values for the cations (5c—i) were then obtained by adjustment of the pK_{R^+} values for the reference cations (5a and b) according to the differences in the $\log([R^+]/[ROH])$ values for solutions in the mixed solvent containing H_2SO_4. This stepping procedure also allowed extension of the H_R^{Fc} scale constructed earlier to solutions containing higher H_2SO_4 concentrations. Values of this acidity function * through the $[H_2SO_4]$ range 0.005—4.00M are in Table 1; it is linearly related to the Deno H_R function [13] for aqueous H_2SO_4 [equation (2)].

TABLE 1

H_R^{Fc} Acidity function [a]

$[H_2SO_4]$/M	0.005	0.010	0.025	0.050	0.100	0.250	0.500
H_R^{Fc}	3.19	2.91	2.51	2.20	1.91	1.60	1.21
$[H_2SO_4]$/M	1.00	1.50	2.00	2.50	3.00	3.50	4.00
H_R^{Fc}	0.60	−0.03	−0.65	−1.27	−1.90	−2.52	−3.15

[a] For solutions in H_2O–MeCN (1 : 1 w/w) at 25.0 °C.

TABLE 2

Rate and equilibrium constants [a]

		H_2O–MeCN		H_2O		
Cation	$\lambda_{max.}$/nm	k_f/s^{-1}	k_r/l mol^{-1} s^{-1}	k_f/s^{-1}	k_r/l mol^{-1} s^{-1}	pK_{R^+}
(5a)	325	62 [b]	15 [b]	44 [c]	135 [c]	0.49
(5b)	360	58 [b]	168 [b]	41 [d]	960 [d]	1.37
(5c)	355	0.90	0.60			0.72
(5d)	440	0.46	2.19			1.58
(5e)	430	0.20	15.9			2.80
(5f)	345	0.58	3.6×10^{-3}			−1.31
(5g)	370	0.86	1.4×10^{-2}			−0.88
(5h)	342	0.24	5.2×10^{-3}			−0.76
(5i)	375	0.32	9.2×10^{-3}			−0.64
(5j)	348	2.66×10^{-2}	37.2			4.08
(5k)	257			55 [e]	3.7 [e]	−1.17
(8)	417	2.50	3.75×10^4			4.18
(9)	327					−2.29
An_3C^+	483	7.4 [f]	8.9 [f]	12 [g]	76	0.82 [g]

[a] At 25.0 °C. [b] 0.125M-H_2SO_4. [c] 0.125M-HCl. [d] 0.0125M-HCl. [e] Extrapolated value (see text). [f] 0.25M-H_2SO_4. [g] Ref. 2*a*.

$$H_R^{Fc} = 1.26H_R + 1.34 \qquad (2)$$

For each of the carbocations (5a—i) and the bridged carbocation (9), plots of $\log([R^+]/[ROH])$ for equilibria in H_2O–MeCN (H_2SO_4) against H_R^{Fc} were linear with slopes in the range 0.97—1.02, demonstrating the generality of this acidity function to these equilibria. The pK_{R^+} values for the very stable diferrocenyl-methyl (5j) and -allyl (8) carbocations were determined for solutions in H_2O–MeCN (HCl) by direct comparison of $\log([R^+]/[ROH])$ *versus* $-\log[\text{acid}]$ plots with that for the reference cation (5b). The value for the relatively unstable primary carbocation (5k) was obtained similarly by direct comparison with (5a) for solutions in aqueous H_2SO_4. The results of all of these pK_{R^+} determinations, related to water as the standard state, are in Table 2.

Rate Measurements.—The rates of reactions with water of the cations (5a, b, and j) and (8), and of the reverse reaction (acid-promoted heterolysis of the alcohols) [reaction (3)] were determined by an equili-

$$R^+ + H_2O \underset{k_r}{\overset{k_f}{\rightleftharpoons}} ROH + H^+ \qquad (3)$$

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* An acidity function $H_R(H_2O\text{–MeCN})$ for triarylmethyl substrates in H_2O–MeCN (1 : 1 w/w) containing H_2SO_4 was similarly constructed using $An_2\overset{+}{C}Ph$ and $An_3\overset{+}{C}$ as indicators; this is also linearly related to the Deno H_R function [equation (i)].

$$H_R(H_2O\text{–MeCN}) = 1.44H_R + 1.12 \qquad (i)$$

brium-displacement method. Typically, an equilibrium mixture of cation and alcohol in H_2O (HCl) or H_2O–MeCN (HCl or H_2SO_4) was diluted with an equal volume of the acid-free solvent, and the rate at which the new equilibrium was established was followed using a stopped-flow spectrometer at the wavelengths (Table 2) of maximum absorbance for the cations (see Experimental section). The reactions were first order (correlation coefficients > 0.999) and the observed first-order rate constants (k_ψ) were separated into k_f and k_r from the relationships (4)—(6).

$$k_\psi = k_f + k_r[H^+] \tag{4}$$

$$K_{R^+} = k_f/k_r = [ROH][H^+]/[R^+] \tag{5}$$

$$k_f = k_\psi/(1 + [H^+]/K_{R^+}) = k_\psi/(1 + [R^+]/[ROH]) \tag{6}$$

Reactions of the cations (5c—i) with water were followed directly in H_2O–MeCN by adding a solution of the tetrafluoroborate salt [15] in MeCN or $(CH_2Cl)_2$ to the reaction solvent and following the disappearance of the cation spectrophotometrically (see Experimental section). Independent experiments established that, under these conditions, the reactions go to completion and cleanly give alcohol. Good first-order rate curves were obtained and the k_f rate constants are in Table 2. Almost identical k_f values were found for experiments in which the cation trifluoroacetates in CF_3CO_2H were added to the mixed solvent containing just sufficient Proton Sponge [*i.e.* 1,8-bis(dimethylamino)naphthalene] to neutralise the acid. The second-order rate constants (k_r) for acid-induced heterolyses of the alcohols (4c—i), calculated from the k_f and K_{R^+} values for the mixed solvent, are also in Table 2. There is a problem in the calculation of k_r for the less basic alcohols (4f—i) because the values of k_f were measured for reactions of the salts in initially neutral media whereas K_{R^+} was determined, of necessity, in high acidic media. We see no simple way of taking into account the effects of these different reaction media which creates uncertainty in our k_r values for these alcohols.

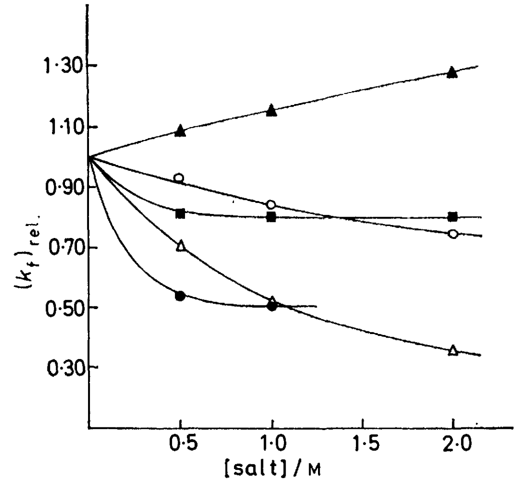

FIGURE 1 Effect of added salts on k_f for addition of water to $\mathrm{Fc\overset{+}{C}HAn}$ in aqueous 0.0125M-HCl: Me_4NCl (▲); LiCl (○); NaCl (■); $NaClO_4$ (△); NaOTs (●)

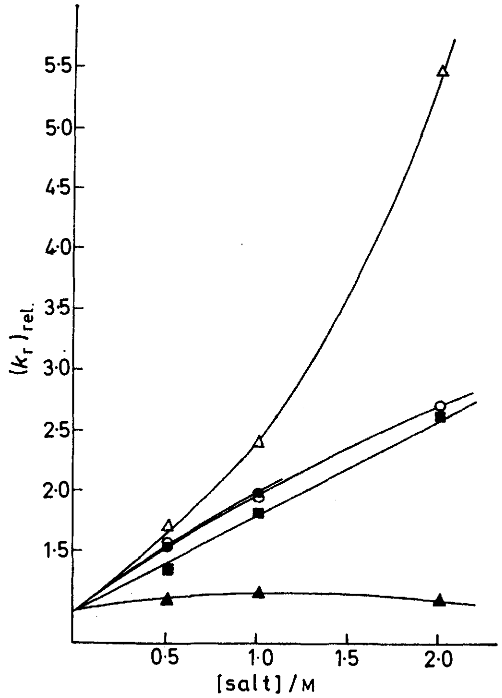

FIGURE 2 Effect of added salts on k_r for heterolysis of FcCH(OH)An in aqueous HCl; key as for Figure 1

Rate constants for the primary system were estimated by mixing a solution of the alcohol (4k) in water with an equal volume of aqueous H_2SO_4 and following the rate of formation of the carbocation (5k) using a stopped-flow spectrometer; k_r values were calculated as before from the k_ψ values and the $[R^+]/[ROH]$ equilibrium ratios at various final acid concentrations. The k_r value was calculated from K_{R^+} (in H_2O) and the k_f value extrapolated to zero $[H_2SO_4]$. However, these results (Table 2) should be regarded with caution since, in order to develop measurable concentrations of (5k) in the kinetic experiments, it was necessary to dilute strong aqueous H_2SO_4 solutions (0.5—2.0M) with an equal volume of water containing (4k). Under these conditions, rates may be significantly affected by the temperature increase due to heat of mixing which may also cause apparent absorbance changes due to a gradient in solution refractive index in the stopped-flow cuvette.

Salt Effects.—Salt effects on k_f and k_r were studied for the secondary system (4b)–(5b). By use of the methods described earlier, we redetermined pK_{R^+} values for equilibria in aqueous HCl containing LiCl, NaCl, $NaClO_4$, NaOTs, and Me_4NCl at various concentrations (0.5—2.0M). From these data and from k_ψ values for equilibrium-displacement reactions in the presence of salt, k_f and k_r were calculated from the expressions given earlier. The effects observed are shown in Figures 1—3. Unfortunately, it was not possible to study kinetic salt effects on reactions of the tertiary carbocations (5c—i) since the corresponding alcohols are insoluble in water

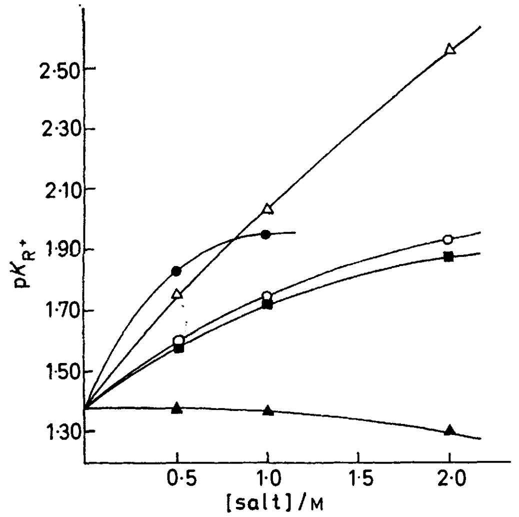

FIGURE 3 Effect of added salts on pK_{R^+} for $Fc\overset{+}{C}HAn$ in $H_2O(HCl)$; key as for Figure 1

and most salts cause separation of the H_2O-MeCN solvent.

Acid-strength Medium Effects.—The effect of added acid upon k_f for water addition was studied for the cation (5f). Solutions of $(5f)(BF_4^-)$ in $(CH_2Cl)_2$ were added to H_2O-MeCN containing H_2SO_4 (0.25—2.0M) and k_f was obtained by correction of k_ψ for cation consumption as described earlier. For the acid concentrations used, the contribution of $k_r[H^+]$ to k_ψ was low (*e.g.* 19.4% for 2.0M-H_2SO_4). The effect of acid on k_f is shown in Figure 4 which also illustrates the corresponding effect for addition of water to (5k) in aqueous H_2SO_4 (from results described earlier).

Solvent Isotope Effects.—The pK_{R^+} values for the cations (5a—i) in D_2O-MeCN (1.11 : 1 w/w; *i.e.* the molar equivalent of the H_2O-MeCN solvent used in related studies) containing D_2SO_4 were estimated from the differences (ΔQ) between log([R$^+$]/[ROH]) values for solutions in D_2O-MeCN (D_2SO_4) and in H_2O-MeCN (H_2SO_4) through a range of acid molarities appropriate for each system [see equation (7)]. For each cation, ΔQ varied little (<0.1 log unit) with change in acid molarity and the averaged values for all the cations were remarkably constant, such that equation (8) holds.

$$\Delta Q = \log([R^+]/[ROD])_{D_2O(D_2SO_4)} - \log([R^+]/[ROH])_{H_2O(H_2SO_4)} \quad (7)$$

$$(pK_{R^+})^D = (pK_{R^+})^H + 0.55\ (\pm\ 0.04) \quad (8)$$

First-order rate constants $(k_f)^D$ for addition of D_2O to the cations (5c—i) in D_2O-MeCN were obtained from experiments, similar to those described earlier, in which $(R^+)(CF_3CO_2^-)$ in CF_3CO_2H was added to the mixed solvent and the disappearance of the cation was followed spectroscopically. The corresponding values for $(k_f)^D$ were calculated as before from $(k_r)^D$ and $(K_{R^+})^D$. The results are in Table 3.

TABLE 3

Solvent isotope effects on rate and equilibrium constants [a,b]

Cation	$(k_f)^D$/ s^{-1}	$(k_r)^D$/ $l\ mol^{-1}\ s^{-1}$	$(k_f)^H/(k_f)^D$	$(k_r)^H/(k_r)^D$	$(K_{R^+})^H/(K_{R^+})^D$
(5a)					3.38
(5b)					3.56
(5c)	0.73	1.70	1.23	0.35	3.51
(5d)	0.38	6.13	1.21	0.36	3.39
(5e)	0.17	44.7	1.18	0.36	3.32
(5f)	0.49	1.05×10^{-2}	1.18	0.34	3.47
(5g)	0.70	3.8×10^{-2}	1.23	0.37	3.31
(5h)	0.20	1.5×10^{-2}	1.20	0.35	3.46
(5i)	0.29	2.8×10^{-2}	1.10	0.33	3.40

[a] At 25.0 °C. [b] Values for D_2O-MeCN (1.11 : 1 w/w) containing D_2SO_4, compared with corresponding values for H_2O-MeCN (1 : 1 w/w) containing H_2SO_4.

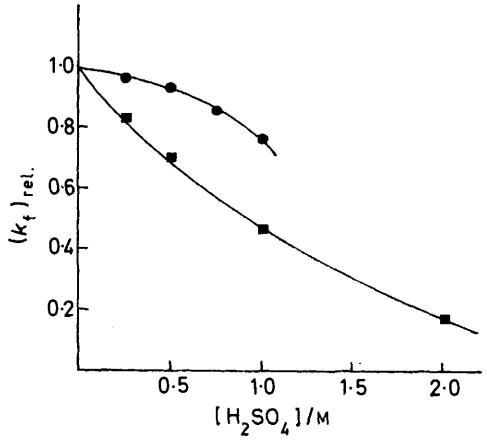

FIGURE 4 Effect of added H_2SO_4 on k_f for addition of water in H_2O-MeCN (1 : 1 w/w) to $Fc\overset{+}{C}(Ph)Bu^t$ (■) and $Fc\overset{+}{C}H_2$ (●)

DISCUSSION

Equilibria.—If it is assumed that differences between the ground-state energies of the alcohols in aqueous media are relatively insignificant,* the variation in the pK_{R^+} values (Table 2) gives an indication of relative thermodynamic stabilities of the carbocations. As expected, progressive substitution of the methylene group of $Fc\overset{+}{C}H_2$ (5k) by aryl groups stabilises the cation with an attenuation of the effect for the second substitution; *cf.* (5k)-(5a)-(5c) and (5k)-(5b)-(5e). However, the magnitude of the effect is much less than for related series, *e.g.* $Ar\overset{+}{C}H_2$-$Ar_2\overset{+}{C}H$-$Ar_3\overset{+}{C}$ (Ar = Ph or An),[17] an indication of the enormous extent to which carbocations are stabilised by the ferrocenyl group. This is further illustrated by the pK_{R^+} values for the series of secondary carbocations (5a)-(5b)-(5j)-(8).

Unexpectedly, substitution of the methinyl hydrogen of $Fc\overset{+}{C}HAr$ (5a and b) by a bulky alkyl group (t-butyl or 1-adamantyl) markedly destabilises the cation [*cf.* (5f—i)], despite the favourable alkyl $+I$ effect. We attribute this apparent anomaly to steric hindrance by

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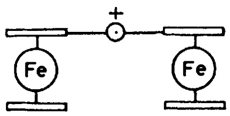
* However, to the extent that steric congestion in the alcohols would be relieved by heterolysis, differences in pK_{R^+} values do not give a true measure of relative carbocation stability.[16]

these bulky groups to coplanarity of the $C_5H_4\overset{+}{C}$ and aryl moieties, thereby reducing π-conjugative stabilisation. This effect is also responsible for the relative instability of the bridged tertiary carbocation (9) [*cf.* (5a)] where steric constraints prevent the interannular bridging group from attaining a conformation which maximises C_5H_4–$\overset{+}{C}$ π-conjugation.[9e]

Introduction of a *p*-methoxy substituent into a phenyl group of the secondary (5a) and tertiary diaryl (5c and d) carbocations stabilises the cation by *ca.* 1 p*K* unit, a resonance effect smaller than that found for triarylmethyl cations; *cf.* $An_2\overset{+}{C}Ph$ (pK_{R^+} −1.24), $An_3\overset{+}{C}$ (pK_{R^+} 0.82).[17b] A *p*-methoxy group is also much less effective in stabilising the tertiary aryl–alkyl carbocations (5f and h), a further indication of attenuated aryl–$\overset{+}{C}$ conjugation in these systems.

Rates.—As is generally the case, the k_f values do not follow pK_{R^+} at all closely. Thus, although reactivity towards water decreases as expected through the carbocation series: primary (5k) > secondary monoaryl (5a and b) > tertiary diaryl (5c—e) > secondary diferrocenyl (5j), the magnitude of the effect is much less than might have been expected [(5b and k) have similar reactivities towards water but differ in stability by *ca.* 2.5 p*K* units], and irregularities are apparent. Furthermore, the bulky alkyl groups whose presence destabilises the cations (5f—i) also cause a decrease in k_f, showing that steric hindrance to nucleophilic addition overcomes any rate enhancement due to steric inhibition of benzylic resonance. In fact, this resonance effect on k_f seems to be of little importance since the values are similar for all the tertiary carbocations (5c—i).



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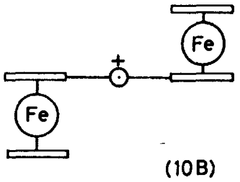

(10B)

Steric hindrance to nucleophilic addition may also be responsible, in part, for the low reactivity of the secondary diferrocenylmethyl cation (5j). It is well established[18] that ferrocenylalkyl cations preferentially add nucleophiles from the *exo*-direction. Of the two conformations (10A) and (10B) of this cation for which resonance stabilisation by both ferrocenyl groups is most effective, the former is disfavoured by a serious non-bonded repulsion between the pendant $Fe(C_5H_5)$ residues. Addition of water to the more favoured *pseudo-trans*-conformer (10B) (see crystal structure[19]) would be correspondingly retarded since nucleophilic approach would of necessity occur from the *endo*-direction with respect to one of the ferrocenyl groups. This interpretation is reinforced by the much higher reactivity of the vinylogous 1,3-diferrocenylallylium cation (8), even allowing for the statistical factor (two equivalent sites for nucleophilic addition).

Introduction of a *p*-methoxy substituent reduces k_f more for the tertiary diaryl cations (5c—e) than for the secondary analogues (5a and b) where the effect is small. Recent ^{13}C n.m.r. spectroscopic studies[20] have suggested that there is significantly greater charge concentration at the formal $\overset{+}{C}$ centre of tertiary as compared with secondary ferrocenylalkyl cations which may account for the observed trend. For the aryl–alkyl systems (5f—i), modest rate enhancements resulting as a consequence of *p*-methoxylation further indicate steric suppression of aryl–$\overset{+}{C}$ π-conjugation such that there may even be an overall electron withdrawal due to the $-I$ effect.

In general, k_r is much more sensitive to substituent effects than is k_f (Table 2). Although the primary alcohol (4k) is much less reactive towards acid-promoted heterolysis than the secondary benzylic alcohols (4a and b), we were surprised to find that these latter compounds are also more reactive than the tertiary analogues (4c—i), particularly the aryl–alkyl substrates (4f—i). Again steric effects appear to be responsible. The presence of two bulky groups, besides ferrocenyl, at the ionisation site causes a reduction in k_r by forcing the conjugate acid of the alcohol into a conformation unfavourable for heterolysis (*exo*-departure of the leaving group is anchimerically assisted[18]) and by inhibiting aryl resonance stabilisation of the transition state. Steric hindrance to departure of the leaving group is also evident in the anomalously low reactivity of diferrocenylmethanol (4j); the secondary vinylogue (6) is more reactive by a factor of *ca.* 10^3.

There are some anomalies in the effects of *p*-methoxylation upon rate and equilibrium constants (Table 2). Whereas introduction of a *p*-methoxy group slightly increases k_f for the cations (5f—i), as noted above, it also stabilises the cation relative to the alcohol (*i.e.* K_{R^+} decreases) and appears to increase k_r. (Problems in estimating k_r from k_f/K_{R^+} have already been indicated.) These anomalies may be due to interactions between the methoxy group and the acidic solvent; it has been shown[21] that interactions between non-ionic solutes and highly acidic media influence ionisation of alkyl halides.

Judged from the properties (Table 2) of the ferrocenylalkyl cations $Fc\overset{+}{C}HAr$ (5a and b) and the tris-*p*-methoxyphenylmethyl cation ($An_3\overset{+}{C}$) in aqueous acid, a change of solvent from H_2O to H_2O–MeCN (1 : 1 w/w) has little influence on the rate of water addition but strongly retards the reverse reaction, *i.e.* the effective acidity of the medium is reduced for the mixed solvent and, for a given acid concentration, the position of equilibrium lies further towards the alcohol which, additionally, is stabilised by the organic solvent.[22]

Added salts (except Me_4NCl) retard the addition of water to the cation (5b) with the effect of LiCl ≈ NaCl < $NaClO_4$ ⩽ NaOTs (Figure 1), but accelerate the reverse reaction with $NaClO_4$ the most effective (Figure 2), and increase H_R^{Fc} as shown by the effect on pK_{R^+} (Figure 3). The quaternary salt (Me_4NCl), on the other hand, causes a modest increase in k_f but has little effect on k_r. These salt effects are generally similar to those found earlier for triarylmethyl substrates[2,17b] and a detailed discussion of their source and nature has been given.[2a] For both systems, anions of low charge density (ClO_4^-, TsO^-) are particularly effective in stabilising the carbocation relative to the transition state for water addition, whereas the relatively hydrophobic Me_4N^+ ion has the opposite effect. In contrast to the behaviour[2a] with $An_3\overset{+}{C}$, however, Li^+ is no more effective than Na^+ in retarding water addition to (5b). Added H_2SO_4 also reduces k_f for addition of water to the primary (5k) and the tertiary (5f) carbocations in H_2O–MeCN, with the medium effect being more marked for the latter (Figure 4).

The observed dependence of k_f and k_r on substrate structure, and their response to medium and salt effects, accord with a carbocation-like transition state, a situation similar to that established for nucleophilic additions to triarylmethyl cations.[1-5] Consistently, relatively small deuterium kinetic solvent isotope effects (Table 3) were found for reactions of the series of cations (5c—i) in $H_2O(D_2O)$–MeCN containing $H_2SO_4(D_2SO_4)$, with an effect on k_f smaller than on k_r: *viz.* $(k_f)^H/(k_f)^D = 1.17 \pm 0.07$; $(k_r)^H/(k_r)^D = 0.35 \pm 0.02$. Although there are considerable uncertainties in the values of k_r for formation of the cations (5f—i), the values of the kinetic and equilibrium isotope effects for these systems agree well with the other values. These effects are very similar to those reported[23] earlier (k^H/k^D values, 1.2 and 0.44, respectively) for corresponding reactions of $An_3\overset{+}{C}$, underlining the close mechanistic similarity between nucleophilic addition reactions of triarylmethyl and ferrocenylalkyl cations.

EXPERIMENTAL

For general remarks concerning synthetic methods, see ref. 24. Acetonitrile (Mallinkrodt Spectrograde) was purified by double distillation from P_2O_5 and the fraction of b.p. 81.5 °C was used. Identical results were obtained using reagent-grade material purified by Coetzee's procedure I.[25] Analytical data, *etc.*, for the new compounds prepared are in Table 4. The ^1H n.m.r. spectra of all ferrocene derivatives used were in accord with the structures assigned.

Preparation of Ketones.—The ketones (1a—e) were prepared by standard Friedel–Crafts reactions between ferrocene and the appropriate acyl chloride in solution in CH_2Cl_2 in the presence of Al_2Cl_6 (see ref. 24 for the general procedure). Compounds (1a),[26] (1b),[26] (1c),[27] and (1e)[28] have been described previously. The *trans*-enone (2)[29] was made by base-catalysed condensation of formyl- and acetyl-ferrocene, and the bridged ketone (3)[30] by the reaction of ferrocene with acryloyl chloride–Al_2Cl_6.

Preparation of Alcohols.—The alcohols (4a),[31] (4b), and (4j)[28] were prepared from the corresponding ketones by reduction with $LiAlH_4$ in ether, the *trans*-propenol (6) by reduction of (2) with $NaBH_4$ in ethanol–tetrahydrofuran, the alcohols (4c),[32] (4d), (4f),[33] (4h), and (7) by addition of PhLi and the alcohols (4e), (4g), and (4i) by addition of AnMgBr to the appropriate ketones in benzene–ether, and the alcohol (4k)[34] by reaction of $FcCH_2\overset{+}{N}Me_3I^-$ with hot aqueous NaOH solution. General procedures for these reactions have been described in the references cited and in ref. 24.

TABLE 4

New compounds

Compound	M.p. (°C)	Formula	Found C (%)	Found H (%)	Required C (%)	Required H (%)
(1d)	142—144	$C_{21}H_{24}FeO$	72.1	6.8	72.4	6.9
(4b)	106—108	$C_{18}H_{18}FeO_2$	67.4	5.7	67.1	5.6
(4d)	*a*	$C_{24}H_{22}FeO_2$	72.3	5.6	72.4	5.6
(4e)	*a*	$C_{25}H_{24}FeO_3$	69.9	5.5	70.1	5.6
(4g)	128—130	$C_{22}H_{26}FeO_2$	70.1	7.0	69.8	6.9
(4h)	*a*	$C_{27}H_{30}FeO$	76.1	7.0	76.1	7.1
(4i)	*a*	$C_{28}H_{32}FeO_2$	73.4	7.0	73.7	7.1
(6)	183—185	$C_{23}H_{22}Fe_2O$	64.7	5.0	64.8	5.2
(7)	146—148	$C_{19}H_{18}FeO$	71.3	5.6	71.7	5.7

[a] Viscous liquid.

Preparation of Tetrafluoroborates of the Cations (4c—i).—A solution of the alcohol (0.5 g) in acetic anhydride–ether (1 : 1; 10 ml) was cooled in an ice-bath and aqueous HBF_4 (45%; 1 ml) was added dropwise with stirring. The solution was stirred at 0 °C for 5 min, then slowly added dropwise to vigorously stirred dry ether (200 ml). The precipitated cation tetrafluoroborate (70—90% yields) was filtered off, washed thoroughly with dry ether, and purified by dissolution in dry alcohol-free CH_2Cl_2 and reprecipitation by dry ether. Samples of these salts were stored in the dark in a refrigerator and were used within 48 h of preparation. Treatment of samples in MeCN with aqueous NaOH gave quantitative yields of the corresponding alcohols.

pK_{R^+} *Measurements.*—Generally, a stock solution (*ca.* 5×10^{-2}M; 0.025 or 0.050 ml) of the alcohol in ethanol was diluted accurately to 10 ml with a standardised solution of HCl or H_2SO_4 in H_2O or H_2O–MeCN (1 : 1 w/w) and the absorbance of the solution at a suitable wavelength (given in Table 2) of maximum absorbance of the cation was recorded for 1 cm cells at 25.0 °C using a Cary 15 spectrometer. For those cations which are unstable in solution, absorbance values were recorded at various intervals following cation generation and the results were extrapolated to zero time. The $[R^+]/[ROH]$ equilibrium ratios were calculated from the absorbances at the appropriate wavelength for solutions containing 100% ROH (no acid) and 100% R^+ (concentrated acid) in the same solvent. For each system, the procedure was repeated for a range of acid concentrations chosen to give $[R^+]/[ROH]$ ratios covering the range 0.1—10. The pK_{R^+} values were calculated from $\log([R^+]/[ROH])$ *versus* $-\log[\text{acid}]$ or H_R^{Fc} plots as indicated in the Discussion section. Duplicate determinations gave good agreement. Determinations for solutions in D_2O–MeCN (D_2SO_4) were carried out using the same procedures and $(pK_{R^+})^D$ values were calculated as described in the Discussion section. The results obtained are in Tables 2 and 3.

Rate Measurements.—For reactions with a half-life > *ca.* 1 s, rates were measured using a Gilford spectrophotometer by addition of a solution (*ca.* 2 µl) of the cation tetrafluoroborate in MeCN or $(CH_2Cl)_2$ to the reaction solvent (*ca.* 3 ml) in a 1 cm cell at 25.0 °C and following the decay with time of a suitable cation absorbance maximum (Table 2). Under these conditions, the reverse reaction is effectively suppressed (very low acid concentration in the final solution). For each system, at least two separate runs were carried out to ensure reproducibility of results. Good first-order $\ln(A_t/A_\infty)$ *versus* t rate plots (correlation coefficients $>$ 0.999) were obtained.

The rates of the faster reactions were followed at 25.0 °C using a Durrum–Gibson stopped-flow spectrophotometer at a suitable wavelength (Table 2) by the procedure previously described.[2a] Repeated determinations gave reproducibly good first-order rate plots in all cases, and rate constants were evaluated as described in the Discussion section. The results are in Tables 2 and 3.

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