

RATES OF ADDITION AND ELIMINATION REACTIONS OF
 FERROCENYLALKYL CATIONS IN AQUEOUS ACETONITRILE: EVIDENCE
 OF ION-PAIR FORMATION AND CHLORIDE-ASSISTED DEPROTONATION

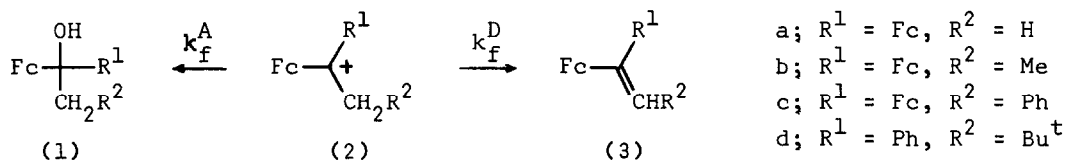
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Summary A kinetic study of concomitant water addition and deprotonation for carbocations of the type $\text{Fc}^+(\text{R}^1)\text{CH}_2\text{R}^2$ has shown that such cations are extensively ion-paired in aqueous acetonitrile; formation of alkene from (R^+Cl^-) ion-pairs is accelerated and from $(\text{R}^+\text{ClO}_4^-)$ ion-pairs is slightly decelerated.

The rôle of ion-pairing in $\text{S}_{\text{N}}1$ solvolyses is well established.¹ However, there is much less information on ion-pairing in additions to preformed carbocations, although potential effects upon rates of nucleophilic addition to triarylmethyl^{2a-c} and ferrocenylalkyl^{2d} cations and of racemisation of chiral ferrocenylalkyl cations³ have been noted. For carbocationic systems which may undergo concomitant addition and elimination, effects of ion-pairing have been inferred only indirectly for $\text{S}_{\text{N}}1$ -E1 reactions of alkyl and bicycloalkyl substrates⁴ where rates of elimination from the carbocation cannot be measured.



We have examined spontaneous reactions of the ferrocenylalkyl cations (2a-d) with water. Rates were measured spectroscopically both for irreversible reactions of the carbocation salts (2)(BF_4^-) with $\text{H}_2\text{O}:\text{MeCN}$ (1:1 w/w) containing 10^{-3}M 4-picoline[†] to suppress completely reverse reactions (i.e. acid heterolysis of

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† Independent experiments established that base catalysis of water addition or of deprotonation is insignificant at this amine concentration.

alcohols, protonation of alkenes), and for reactions of the carbocations with the same solvent containing HCl or HClO_4 which gave equilibrium mixtures of cation (2) and alkene (3).[‡] The first-order rate constants for water addition (k_f^A) and for deprotonation (k_f^D) were calculated from the observed first-order rate constants (k_ψ) for carbocation consumption and the alcohol/alkene product ratios (determined spectroscopically) for the irreversible reactions, and from the carbocation/alkene equilibrium ratios for reactions in acidic solvent using the relationship:

$$k_f^D = k_\psi / 1 + \{[(2)] / [(3)]\}_{\text{eq}}$$

These experiments were repeated with the same solvent containing NaCl or NaClO_4 and the individual rate constants were separated as before. Typical results are in the Table and Figure.

The k_f^A values for water addition decrease through the series (2a) > (2b) > (2c) > (2d) because of steric hindrance by the increasingly bulky β -substituent (R^2). This effect is particularly marked for the neopentyl substrate (2d) whose rate of deprotonation is also much slower than those of the diferrocenylalkylm ions (2a-c). Surprisingly, the ethyl substrate (2b) deprotonates more slowly than its methyl analogue (2a). The relatively small increase in the rate of deprotonation of the benzyl substrate (2c) suggests that π -conjugative stabilisation by the β -phenyl group of the double bond developing in the transition state is strongly attenuated by twisting imposed by steric repulsion of the vicinal ferrocenyl group (cf. crystal structure⁵).

Under irreversible reaction conditions in the absence of added salts, the methyl and ethyl substrates (2a,b) give >90% addition, whereas the benzyl and neopentyl analogues (2c,d) give similar amounts of addition and elimination (cf. k_f^A and k_f^D values). As for triarylmethyl cations^{2a} added NaCl or NaClO_4 at concentrations $\leq 0.5\text{M}$ do not markedly retard addition of water to the cations (2) but substantially accelerate acidic heterolysis of the alcohols (1). Unexpectedly, however, added Cl^- (as HCl or NaCl) sharply speeds deprotonation of the cations. Because HCl is a strong acid in our solvent,⁶ this effect is not due to Cl^- acting as an external basic catalyst. Furthermore, although added ClO_4^- (as HClO_4 or NaClO_4) has itself little decelerating effect upon deprotonation rates, it substantially reduces the rate-accelerating effect of Cl^- . Typical results are illustrated in the Figure for reactions of the cation (2b); the other cations behave similarly.

These findings cannot be due simply to the medium effects of the anions in solution, and they show that Cl^- and ClO_4^- must compete for the carbocations. It follows that the cations (2) must be extensively ion-paired in aqueous MeCN but only the (2)(Cl^-) pairs rapidly give alkene. One explanation is that Cl^- in the ion-pair (but not ClO_4^-) is sufficiently basic to assist proton loss from the cation; such an effect has been proposed^{4a} for concomitant $\text{S}_{\text{N}}1$ -E1 reactions of

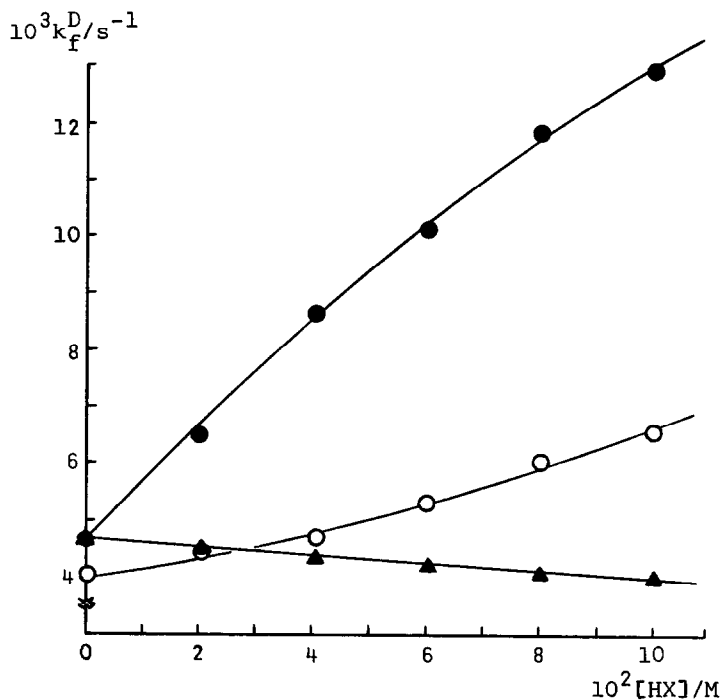
[‡] Under these conditions, the equilibrium concentrations of the alcohols (1) are very small.

Table. Typical rate constants for reactions of the salts (2)(BF₄⁻) with H₂O:MeCN (1:1 w/w) at 25.0°C^a

Carbocation	[NaCl]/M	[NaClO ₄]/M	10 ² k _f ^A /s ⁻¹	10 ² k _f ^D /s ⁻¹
(2a)	-	-	20.	1.0
	0.20	-	16.	7.5
	-	0.20	15.	ca. 1.
(2b)	-	-	11.	0.47
	0.20	-	10.	1.9
	-	0.20	8.0	0.40
(2c)	-	-	5.4	2.8
	0.20	-	2.4	10.4
	-	0.20	3.9	2.4
(2d)	-	-	0.031	0.049
	0.20	-	0.013	0.19
	-	0.20	0.019	0.040

^aRates were measured using a Gilford spectrophotometer for reactions of (2)(BF₄⁻) (ca. 5 × 10⁻⁵M) with solvent containing 4-picoline (10⁻³M), following the disappearance of the carbocation absorbances at 655 nm (2a), 720 nm (2b), 735 nm (2c), and 338 nm (2d).

Figure. Variation in k_f^D values for deprotonation of the cation (2b) at 25.0°C in H₂O:MeCN (1:1 w/w) containing HCl (●), HClO₄ (▲), and HCl + 0.20M NaClO₄ (○).



alkyl substrates. Added Br^- also assists deprotonation of the cations (2), but less effectively than Cl^- .

Conformational effects may also be important. We have previously shown⁷ that proton loss from $\text{Fc}\overset{\dagger}{\text{C}}(\text{R}^1)\text{CHR}^2\text{R}^3$ occurs preferentially from the exo-face of the fulvene-like ligand (i.e. in the direction anti to the Fe atom). Consequently, changes in the populations of the various conformers of the cations (2) induced by ion-pairing may speed deprotonation. In this hypothesis, we ascribe the different kinetic behaviour of cations paired with Cl^- and ClO_4^- to the disparate steric bulk of these anions; e.g. although both must pair with the cations, the much bulkier ClO_4^- may hinder loss of a proton, probably by excluding water molecules from its vicinity, whereas the smaller Cl^- does not have this adverse effect.

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