A Kinetic Study of Concomitant Addition and Deprotonation Reactions of Ferrocenyl-stabilised Carbocations in Aqueous Acetonitrile and of the Reverse Reactions

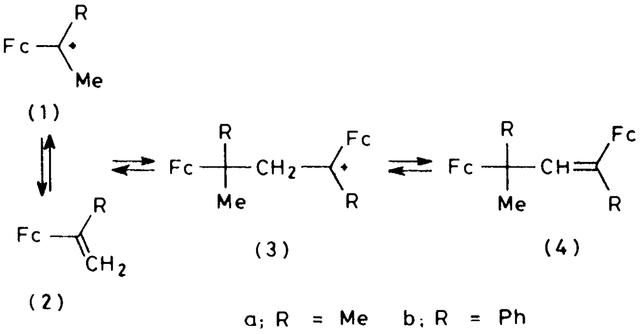
By **Clifford A. Bunton** * and **Nelson Carrasco,** Department of Chemistry, University of California, Santa Barbara, California 93106, U.S.A.
Norman Cully and **William E. Watts,*** School of Physical Sciences, New University of Ulster, Coleraine, Northern Ireland BT52 1SA

Rate constants for addition of water and for deprotonation in aqueous acetonitrile have been measured for a series of ferrocenyl-stabilised carbocation salts. Both alcohol and alkene are formed from $Fc\overset{+}{C}(Ph)CH_2R$ (Fc = ferrocenyl; R = Ph and Bu^t) and $Fc_2\overset{+}{C}CH_2Ph$, but $Fc\overset{+}{C}(Ph)CH_2CPh_3$ reacts exclusively by deprotonation and $Fc_2\overset{+}{C}CH_2R$ (R = H and Me) mainly (>90%) by addition. Bulky β-substituents (Bu^t and CPh_3) retard both reactions by steric and conformational effects which disfavour addition and proton loss. The usual rate-accelerating effect of a β-phenyl group upon deprotonation is strongly attenuated by steric hindrance to styryl conjugation. Rates of water addition and deprotonation are slowed by perchlorate ions (from $NaClO_4$ or $HClO_4$). Chloride ions (from NaCl or HCl) retard water addition but substantially accelerate deprotonation; the magnitude of the latter effect is reduced in the presence of perchlorate ions showing that ion-pairing must be extensive and that both anions compete for carbocations, with rates of elimination from the $(R^+)(Cl^-)$ ion-pairs enhanced. At a given acidity, diferrocenylalkanols $Fc_2C(OH)CH_2R$ undergo acid heterolysis in aqueous acetonitrile faster than the monoferrocenyl substrates $FcC(Ph)(OH)CH_2R$, but there is no obvious correlation between these rates and those for water addition to the resulting carbocations. For a given acidity and solvent, protonation of the alkenes $FcC(R^1) = CHR^2$ is faster for the diferrocenyl (R^1 = Fc) than for the monoferrocenyl compounds (R^1 = Ph), and is slowed when R^2 is phenyl or t-butyl. Rates of both alcohol heterolysis and alkene protonation are increased by chloride and perchlorate ions and by an increase in the water content of the solvent from 1 : 1 to 3 : 1 w/w H_2O–MeCN.

ALTHOUGH rates of nucleophilic additions to preformed carbocations (*e.g.* triarylmethyl and tropylium cations) have been studied extensively,[1] no such systems are available for study of deprotonation.[2] Relevant information comes indirectly from alkene : addition product ratios for concomitant S_N1–$E1$ reactions of alkyl and bicycloalkyl substrates,[3] where rates of elimination from the intermediate carbocations or ion-pairs cannot be measured. However, these studies showed that the relative rates of competing addition and deprotonation are sensitive to solvent, medium, and counter-ion.

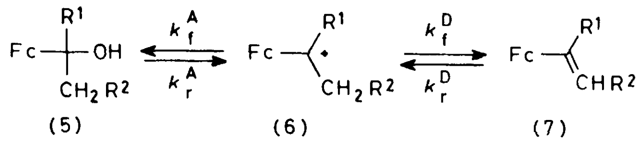
Many ferrocenyl-stabilised carbocations are available,[4] including those which undergo deprotonation, and we have reported [5] kinetic studies of nucleophilic additions and of the reverse reactions. Stereochemical studies have established [4] that these reactions proceed by preferential addition of the nucleophile to the *exo*-face of the pentafulvene-like ligand of the cation (*i.e.* from the direction *anti* to the iron atom) and we have recently shown [6] that deprotonation involves preferential *exo*-proton transfer, in the absence of adverse steric factors. Steric effects are clearly important in eliminations from ferrocenylalkyl cations, and anti-Saytzeff alkenes are often the predominant products.[7]

Study of deprotonation of ferrocenylalkyl cations is occasionally complicated by the nucleophilicity of the resulting alkenes which allows addition of unconsumed carbocation. For example, 1-ferrocenylethylium ions (1) may add to the related terminal alkenes (2) at rates competitive with those for their deprotonation (Scheme 1).[8] The new carbocations (3), which have very similar electronic absorption spectra to those of their precursors (1), undergo slow deprotonation to the alkenes (4) because of steric hindrance to proton transfer (see later). This problem prevents measurement of the rates of deprotonation of carbocations such as the 1-methylethyl (1a) and 1-phenylethyl (1b) species. However, the increased steric hindrance associated with coupling of the 1,1-diferrocenyl substrates (1 and 2; R = Fc) suppresses this side-reaction. Cation + alkene coupling is also hindered by the presence of a substituent at the β-carbon, and kinetic study of deprotonation of cations of the type (6; $R^2 \neq H$) can be carried out without complication.



SCHEME 1

In this paper, we report a study [9] of the rates of addition and deprotonation (Scheme 2) for the carbocations (6a—f), and of the reverse reactions. Preparations of the tetrafluoroborates of these cations and of the alcohol (5) and alkene (7) precursors are in the Experimental section. Because of the low solubility of the neutral products in water, reactions were carried out in H_2O–MeCN (1 : 1 w/w). Rate constants for addition of water to a range of non-deprotonatable ferrocenyl-stabilised carbocations in this solvent have been measured.[5]



(5) (6) (7)

a; $R^1 = R^2 = Ph$
b; $R^1 = Ph, R^2 = CPh_3$
c; $R^1 = Ph, R^2 = Bu^t$
d; $R^1 = Fc, R^2 = H$
e; $R^1 = Fc, R^2 = Me$
f; $R^1 = Fc, R^2 = Ph$

SCHEME 2

RESULTS

Irreversible Reactions.—The spontaneous reactions of of the salts (6a—f)(BF_4^-) with H_2O–MeCN (1 : 1 w/w) at 25.0 °C were followed spectroscopically (see Experimental section). The first-order rate constants (Scheme 2) for water addition (k_f^A) and deprotonation (k_f^D) were calculated from the observed first-order rate constant (k_ψ) for carbocation consumption: $k_\psi = k_f^A + k_f^D$ and $k_f^A = k_\psi/(1 + [\text{ene}]/[\text{ROH}])$ where [ene]/[ROH] is the molar ratio of alkene (7) and alcohol (5) formed under kinetic control. However, because the carbocations (6d and e) react mainly (>90%) by addition, better estimates of the k_f^D values for these substrates were obtained by another method (see later). The highly hindered carbocation (6b) reacts exclusively by deprotonation (*i.e.* $k_\psi = k_f^D$). Because the alcohols (5d—f) resulting from addition of water to the corresponding cations (6d—f) readily undergo acid-promoted dehydration in the dilute HBF_4 (*ca.* 5×10^{-5}M) generated upon solvolysis, reactions of the salts (6d—f)(BF_4^-) were conducted in the presence of 4-picoline to suppress alcohol heterolysis. Independent experiments[10] established that base catalysis of water addition or deprotonation is insignificant at the amine concentrations used ($\leqslant 10^{-3}$M). Methods for determination of the [ene]/[ROH] kinetic product ratios are described in the Experimental section, and the rate constants are in Table 1.

TABLE 1

First-order rate constants for water addition and deprotonation in reactions of the salts (6) (BF_4^-) in aqueous acetonitrile[a]

Cation	R^1	R^2	Solvent[b]	Salt (concentration/M)	$10^2k_f^A/s^{-1}$	$10^2k_f^D/s^{-1}$[c]
(6a)	Ph	Ph	1 : 1		26.0	13.0
(6b)	Ph	CPh_3	1 : 1		<0.0008	0.081
(6c)	Ph	Bu^t	1 : 1		0.031	0.049
			1 : 1	$NaClO_4$ (0.20)	0.019	0.040
			1 : 1	NaCl (0.20)	0.013	0.192
(6d)	Fc	H	1 : 1		20.0	(2.0)
			1 : 1	$NaClO_4$ (0.20)	15.1	(1.5)
			1 : 1	NaCl (0.20)	18.6	(4.0)
			3 : 1		16.3	(3.0)
			3 : 1	$NaClO_4$ (0.20)	11.5	(2.0)
			3 : 1	$NaClO_4$ (0.50)	8.8	(2.0)
			3 : 1	NaCl (0.20)	13.5	5.6
			3 : 1	NaCl (0.50)	11.5	6.9
(6e)	Fc	Me	1 : 1		10.6	(0.5)
			1 : 1	$NaClO_4$ (0.20)	7.6	(0.5)
			1 : 1	NaCl (0.20)	9.8	(3.0)
(6f)	Fc	Ph	1 : 1		5.4	3.0
			1 : 1	$NaClO_4$ (0.20)	3.9	2.5
			1 : 1	NaCl (0.20)	4.8	11.3

[a] At 25.0 °C; values determined as described in text; reactions of (6d—f) were conducted in the presence of 10^{-3}M-4-picoline. [b] Proportions (w/w) of H_2O–MeCN, respectively. [c] Values in parentheses are approximate (see text); better values are in Table 4.

Reactions of the salts (6c—f)(BF_4^-) were also examined in H_2O–MeCN (1 : 1 w/w) containing NaCl and $NaClO_4$, again in the presence of 4-picoline. Values of k_f^A and k_f^D were obtained as before from the observed first-order rate constants (k_ψ) for carbocation consumption and the [ene]/[ROH] kinetic product ratios; typical results are in Table 1. We also investigated solvent effects by determination of k_f^A and k_f^D (Table 1) for reactions of (6d)(BF_4^-) in H_2O–MeCN (3 : 1 w/w) containing 4-picoline with and without NaCl or $NaClO_4$. The products derived from the other carbocations are too insoluble in this more aqueous solvent to permit kinetic measurements. However, higher inorganic salt concentrations (up to 0.5M) could be used without solvent phase-separation, which occurs at > *ca.* 0.25M salt for the 1 : 1 w/w solvent.

Acid Heterolysis of the Alcohols.—Reactions of the alcohols (5) with aqueous acid were also studied. For reactions of (5a) in H_2O–MeCN (1 : 1 w/w) containing H_2SO_4 (>0.1M), deprotonation of the carbocation (6a) is much faster than its production by heterolysis of the alcohol and its concentration does not build up significantly during the reaction. Under these conditions, the observed first-order rate constant (k_ψ) for formation of the alkene (7a) at a particular acid concentration is given by equation (1). Values of $k_r^A[H^+]$ could then be

$$k_\psi = k_f^D k_r^A[H^+]/(k_f^D + k_f^A) \qquad (1)$$

evaluated on the assumption that the kinetic product ratio (k_f^D/k_f^A 0.5) determined previously (Table 1) for reaction of (6a)(BF_4^-) with H_2O–MeCN (1 : 1 w/w) is unaffected by dilute acid. Earlier work has shown[5a] that H_2SO_4 is a monoprotonic acid in H_2O-MeCN (1 : 1 w/w) over the range of concentrations used (0.1—0.5M), and k_r^A calculated from $k_r^A[H^+]/[H_2SO_4]$ was essentially constant over this acid range (Table 2).

Reactions of the alcohols (5c—f) with acid showed quite different kinetic behaviour from that of (5a). At the acid concentrations used, these heterolyses are much faster than deprotonations of the resulting carbocations (6c—f) such that, in effect, alcohol and carbocation are in equilibrium. The first-order rate constants (k_ψ) for build-up of carbocation under these conditions are given by equation (2). Plots of k_ψ against $[H^+]$ for reactions

$$k_\psi = k_f^A + k_r^A[H^+] \qquad (2)$$

with HCl were reasonably linear for $[H^+] \leqslant 0.2$M, and extrapolation to zero [HCl] gave values of k_f^A in good agreement with those determined previously (Table 1). These earlier values are the more accurate because, under the conditions of the alcohol heterolysis experiments, $k_r^A[H^+] \gg k_f^A$. Values of k_r^A obtained from the slopes of these plots are in Table 2.

TABLE 2

Second-order rate constants for acid heterolysis of alcohols (5) in aqueous acetonitrile [a]

Alcohol	R^1	R^2	Solvent [b]	Acid	Concentration range (M) [c]	k_r^A/l mol^{-1} s^{-1}
(5a)	Ph	Ph	1 : 1	H_2SO_4	0.1—0.5	0.097
(5c)	Ph	Bu^t	1 : 1	H_2SO_4	0.1—0.5	0.21
			1 : 1	HCl	0.025—0.5	0.24
			1 : 1	$HClO_4$	0.01—0.05	0.23
(5d)	Fc	H	1 : 1	HCl	0.005—0.05	284.0
			1 : 1	$HClO_4$	0.005—0.02	350.0
(5e)	Fc	Me	1 : 1	HCl	0.02—0.2	80.5
			1 : 1	$HClO_4$	0.02—0.05	111.0
			3 : 1	HCl	0.025—0.15	227.0
			3 : 1	$HClO_4$	0.02—0.10	252.0
(5f)	Fc	Ph	1 : 1	HCl	0.05—0.2	17.7
			1 : 1	$HClO_4$	0.08—0.1	28.6

[a] At 25.0 °C; values determined as described in text. [b] Proportions (w/w) of H_2O–MeCN, respectively. [c] Range of acid concentrations through which plots of k_ψ against [acid] are linear (see text).

TABLE 3

Rate constants for reactions of alcohol (5c) with $HClO_4$ in the absence and presence of salts [a]

	No salt		$NaClO_4$ (0.10M)		NaCl (0.10M)	
$[HClO_4]$/M	10^2k_ψ/s^{-1}	k_r^A/l mol^{-1} s^{-1}	10^2k_ψ/s^{-1}	k_r^A/l mol^{-1} s^{-1}	10^2k_ψ/s^{-1}	k_r^A/l mol^{-1} s^{-1}
0.01	0.296	0.23 [b]	0.405	0.32 [b]	0.390	0.23 [b]
0.02	0.534		0.761		0.622	
0.04	0.991		1.37		1.10	
0.06	1.56		2.00		1.54	
0.08	2.25		2.78		2.05	
0.10	2.88		3.82		2.72	

[a] At 25.0 °C in H_2O–MeCN (1 : 1 w/w). [b] From the slope of the plot of k_ψ against $[HClO_4]$ for $[H^+] \leqslant 0.04$M.

However, values of k_ψ for reactions of the less reactive alcohols (5c and f) at higher concentrations of HCl (0.2—0.5M) were higher than predicted by linear extrapolation from values for the lower acid concentrations. Similarly, plots of k_ψ against $[H^+]$ for reactions of the alcohols (5c—f) with $HClO_4$ showed systematic upward curvature which became more pronounced with increasing acid concentration. Estimates of k_r^A from the slopes of these plots for the lower acid concentrations (which approached linearity and gave intercepts at zero $[HClO_4]$ close to the expected k_f^A values) gave for the alcohols (5d—f) values of k_r^A appreciably higher than those found for reactions with HCl.

Deviations of these k_ψ *versus* $[H^+]$ plots from linearity arise because k_f^A and k_r^A are sensitive to the nature and concentration of anions present in the kinetic solutions. This effect is illustrated by the results of experiments in which k_ψ values were determined as before for reactions of the alcohol (5c) with $HClO_4$ in H_2O–MeCN (1 : 1 w/w) in the presence of 0.1M-NaCl and 0.1M-$NaClO_4$, separately. At each acid concentration (0.01—0.10M), k_ψ was larger for reaction in the presence of $NaClO_4$ compared with that of NaCl (which has little effect on k_ψ) and the difference increased with increasing acid concentration (and hence increasing $[ClO_4^-]$). These results are in Table 3.

The solvent effect upon k_r^A was studied for reaction of the alcohol (5e) with HCl and $HClO_4$ in H_2O–MeCN (3 : 1 w/w). Comparison of the results (Table 2) with those for the corresponding earlier experiments in the 1 : 1 w/w solvent showed that, for both acids (0.02—0.2M), alcohol heterolysis proceeds *ca.* 2.5 times faster in the more aqueous solvent.

Protonation of the Alkenes.—The base strengths of the alkenes (7) differ remarkably. Thus, whereas relatively concentrated acid (*e.g.* 4M-H_2SO_4) slowly and only partially protonates the ferrocenylstilbene (7a), 1,1-diferrocenylethene (7d) is rapidly and extensively (>90%) protonated by 0.1M-HCl in aqueous acetonitrile.

Rates of attainment of alkene $\rightleftharpoons$ carbocation equilibria were determined by addition of the more basic alkenes (7c—f) or the (BF_4^-) salts of the corresponding carbocations (6c—f) to H_2O–MeCN (1 : 1 w/w) containing HCl, $HClO_4$, or H_2SO_4, and following absorbance of carbocation (see Experimental section). The equilibrium concentrations (*cf.* Scheme 2) of the alcohols (5c—f) in these acidic solutions are negligible. Salt effects on rates were investigated in similar experiments with the alkenes (7c, e, and f) and related carbocation salts in the same solvent containing HCl and $HClO_4$ with added NaCl, $NaClO_4$, or NaBr. The solvent effect was studied for reactions of (7d) and (6d)(BF_4^-) with HCl and $HClO_4$ in H_2O–MeCN (3 : 1 w/w).

TABLE 4

Rate constants for protonation of the alkenes (7) and for deprotonation of the cations (6) in aqueous acetonitrile [a]

Alkene	R^1	R^2	Solvent [b]	Acid	[Acid]/M	Salt [c]	$10^2k_f^D$/ s^{-1}	$10^2k_r^D$/ $l\ mol^{-1}\ s^{-1}$
(7c)	Ph	Bu^t	1 : 1	H_2SO_4	0.25		0.053	0.0108
			1 : 1	H_2SO_4	0.50		0.043	0.0106
(7d)	Fc	H	1 : 1	HCl	0.01—0.1		1.0	148.0
			1 : 1	$HClO_4$	0.01—0.1		1.1	126.0
			3 : 1	HCl	0.01—0.08		3.2	266.0
			3 : 1	$HClO_4$	0.01—0.08		2.8	396.0
(7e)	Fc	Me	1 : 1	HCl	0.01—0.2		0.49	
			1 : 1	$HClO_4$	0.01—0.1		0.46	
			1 : 1	HCl	0.10		1.29	3.48
			1 : 1	HCl	0.10	$NaClO_4$	0.65	4.48
			1 : 1	HCl	0.10	NaCl	2.62	6.04
			1 : 1	$HClO_4$	0.10		0.43	1.96
			1 : 1	$HClO_4$	0.10	$NaClO_4$	0.34	2.75
			1 : 1	$HClO_4$	0.10	NaCl	1.18	4.88
(7f)	Fc	Ph	1 : 1	HCl	0.04—0.2		3.95	
			1 : 1	$HClO_4$	0.01—0.1		2.60	
			1 : 1	HCl	0.20		10.4	2.40
			1 : 1	HCl	0.20	$NaClO_4$	4.9	3.45
			1 : 1	HCl	0.20	NaCl	18.2	3.80
			1 : 1	$HClO_4$	0.20		2.37	1.85
			1 : 1	$HClO_4$	0.20	$NaClO_4$	1.94	2.60
			1 : 1	$HClO_4$	0.20	NaCl	4.72	3.30

[a] At 25.0 °C; values determined as described in text. [b] Proportions (w/w) of H_2O–MeCN, respectively. [c] Salt concentration 0.20M.

Under the conditions of these experiments, equation (3) holds where k_ψ, k_f^D, and k_r^D are, respectively, the first-

$$k_f^D = k_\psi - k_r^D[H^+] = k_\psi/\{1 + ([R^+]/[ene])_{eq}\} \quad (3)$$

order rate constants for alkene $\rightleftharpoons$ carbocation equilibration and for carbocation deprotonation, and the second-order rate constant for alkene protonation, and $([R^+]/[ene])_{eq}$ is the equilibrium molar ratio of carbocation and alkene for a given acid concentration. Extrapolation of plots of k_ψ against $[H^+]$ to zero acid gave good estimates of k_f^D for the cations (6c – f); these values are in Table 4. However, the rate constants k_f^D and k_r^D are sensitive to the nature and concentration of anions in the kinetic solutions (see later), and the corresponding plots were linear only up to *ca.* 0.1M-acid. Estimates of k_r^D for the most basic alkene (7d) from the slopes of these plots are in Table 4.

The k_f^D and k_r^D values for reactions at higher acid concentrations and in the presence of inorganic salts were calculated from the relationships given earlier by determination (see Experimental section) of the $[R^+]/[ene]$ equilibrium ratios at the various acid concentrations. The results (Table 4) show that, while perchlorate ions mildly retard deprotonation of the carbocations, this reaction is substantially accelerated by chloride ions. Both anions speed protonation of the alkenes. Increase in the water content of the solvent increases both k_f^D and k_r^D for interconversion of (6d) and (7d).

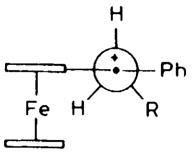
DISCUSSION

Stereochemical and Conformational Factors.—In principle, deprotonation of the carbocations (6a—c) can give *E*- and *Z*-stereoisomers of the alkenes (7a—c). The ^1H n.m.r. spectra (see Experimental section) of these products, formed under non-equilibrating conditions, suggest that only one stereoisomer of the alkenes (7b and c) is formed, whereas reactions of the carbocation (6a) afford both stereoisomers, with the *E*-alkene [11] (*i.e.* Fc and Ph *trans*) predominant (*ca.* 90%). This may arise by kinetically favoured *exo*-deprotonation [6] of the cation in the conformation (8A; R = Ph) which is very much less crowded than the alternative (8B; R = Ph) which has severe steric repulsion between the β-phenyl and $Fe(C_5H_5)$ residues; *exo*-proton transfer is precluded for the least crowded conformation (8C; R = Ph).

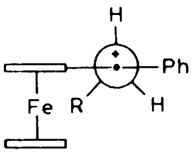
Increase in steric bulk of the β-substituent (R) progressively disfavours the conformations (8A) and particularly (8B) such that the carbocations (6b and c) may undergo substantial or exclusive *endo*-deprotonation in the least crowded conformation (8C; R = CPh_3 and Bu^t, respectively). Transfer to a base of the structurally more accessible methylene proton of (8C) would presumably give the *E*-stereoisomer of the alkene, but the structures of the products (7b and c) have not been established.

Rates of Addition.—Rates of nucleophilic additions to ferrocenyl-stabilised carbocations are sensitive to steric factors [5] which may attenuate *pπ–pπ* conjugation of the formal C$^+$ centre with attached substituents (*e.g.* aryl, Fc) with increase in cation electrophilicity, or introduce steric hindrance to nucleophilic attack. The latter effect is particularly important for neutral nucleophiles such as bulky amines or water where there is appreciable bond-making in the transition states for addition.[5b]

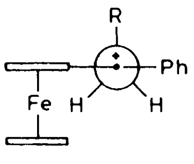
As indicated earlier, ferrocenylalkyl cations undergo preferential *exo*-addition of nucleophiles.[4] In the strongly favoured conformation (8C) of the cations (6b and c), the bulky group (R = CPh$_3$ and Bu^t, respectively) effectively shields the reaction site from nucleophilic attack from the *exo*-direction, and water addition is very hindered (*cf.* k_f^A values; Table 1). Nucleophilic addition to ferrocenylvinyl cations of the type (9) is similarly very strongly retarded by the fixed *exo*-t-butyl group.[12] In this connection, it is noteworthy that a β-t-butyl group provides much greater steric hindrance to addition than an α-t-butyl group, as is evident from inspection of Dreiding models; under the same reaction conditions, addition of water to Fc$\overset{+}{C}$(Ph)-Bu^t occurs *ca.* 2 000 times faster [5a] than to the neopentyl analogue (6c). Much less steric hindrance is provided by a β-phenyl group and the rate constant (Table 1) for water addition to (6a), which may react in conformation (8A), is similar to those for reactions [5a] of diaryl(ferrocenyl)methyl cations (k_f^A 0.6 ± 0.4 s^{-1}).



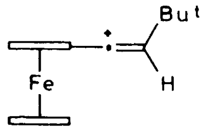
(8A)



(8B)



(8C)



(9)

The reactivities of the 1,1-diferrocenylalkyl cations Fc$_2\overset{+}{C}$R (6d—f) towards water addition decrease with increasing steric bulk of R, *i.e.* R = Me > Et > CH$_2$Ph (Table 1), suggesting increasing steric hindrance towards nucleophilic attack. However, these tertiary carbocations are all *more* reactive towards water than the secondary analogue Fc$_2\overset{+}{C}$H (k_f^A 0.027 s^{-1}).[5a] Typically, secondary alkyl carbocations are more reactive than tertiary towards nucleophilic addition,[13] but exceptions to this behaviour have been found [5] earlier with ferrocenylalkyl cations. We believe that conformational effects are very important. From a comparative study [5b] of the reactivities of a series of ferrocenylalkyl and triarylmethyl cations towards a range of neutral and anionic nucleophiles, it was concluded that Fc$_2\overset{+}{C}$H reacts preferentially in a *syn*-conformation in which steric repulsions between the Fc groups are minimised by bending and twisting of the (C$_5$H$_4$)$\overset{+}{C}$H(C$_5$H$_4$) ligand from a coplanar geometry. Such twisting, which reduces the effectiveness of Fc–C$^+$ conjugative stabilisation, would be reinforced by replacement of the methine hydrogen ($\overset{+}{C}$H) by an alkyl group R because of additional steric repulsions between R and the two adjacent hydrogens attached to the α-positions of coplanar C$_5$H$_4$ rings. Thus, the higher reactivity of the tertiary carbocations (6d—f) towards water may reflect diminished conjugative stabilisation by the two Fc groups, compared with the situation which obtains with the secondary diferrocenylmethyl cation. This steric inhibition of resonance is more important than steric hindrance to water addition by the CH$_2$R group, except for (6b) where R is very bulky. Other evidence bearing on the importance of conformational effects comes from the rates [5a] of acid-catalysed conversion of 1-ferrocenylalkanols into ferrocenylalkyl cations, where secondary alcohols are often more reactive than tertiary.

Addition of water to the cations (6c—f) is retarded by NaCl and NaClO$_4$ (*cf.* k_f^A values; Table 1), as found for reactions of triarylmethyl [1b] and other ferrocenylalkyl [5a] cations. Increase in the water content of the aqueous acetonitrile solvent from 1 : 1 to 3 : 1 w/w causes small reductions (by *ca.* 22 ± 5%) of the rate constants (Table 1) for water addition to (6d) both in the presence and absence of added inorganic salts.

Rates of Deprotonation.—The reactivities of the carbocations (6) towards deprotonation in H$_2$O–MeCN (1 : 1 w/w) cover a *ca.* 250-fold change and decrease in the order (6a) > (6f) > (6d) > (6e) > (6b) > (6c). We have recently found [10] that there is a β-deuterium kinetic isotope effect of *ca.* 3.8 (k^{CH_2}/k^{CD_2}) for spontaneous deprotonation of the carbocation (6c) in aqueous acetonitrile, suggesting a transition state in which proton transfer is significantly advanced and some carbon–carbon double-bond character has developed.* The enhanced rates of deprotonation of the cations (6a and f) compared with the other substrates (*cf.* k_f^D values; Tables 1 and 4) may then be due to resonance stabilisation by the β-phenyl group of the double bond developing in the transition state. However, the relatively small magnitude of the rate effect [*cf.* the benzyl substrate (6f) is only about three times more reactive than the methyl analogue (6d)] suggests that π-conjugation of the β-phenyl group is strongly attenuated by twisting imposed by steric repulsion of the vicinal phenyl or ferrocenyl group [*cf.* crystal structure [11] of *Z*-(7a)].

At the other extreme of reactivity, the very slow deprotonation of the cations (6b and c) (Table 1) can be attributed to the bulky β-substituent (CPh$_3$ and Bu^t, respectively) causing steric hindrance to proton transfer to a water molecule and perhaps imposing a conformation

---

* The primary kinetic isotope effect will be slightly less than 3.8, because there will be a small (*ca.* 10%) contribution of a secondary isotope effect.

(8C) which demands the kinetically less favourable[6] *endo*-deprotonation.

Whereas deprotonation of the carbocations (6c—f) is slightly retarded by $NaClO_4$, added NaCl sharply increases k_f^D. This rate enhancement is due specifically to halide anions (*cf.* later experiments with NaBr); thus, k_f^D values (Table 4) for reactions in aqueous acidic acetronitrile in the absence of inorganic salts also increase with increasing [HCl] whereas a small decrease is found with increasing [$HClO_4$]. These effects are illustrated in Figure 1 for reactions of (6f) whose behaviour is typical of the series (6c—f). The relationships between k_f^D and $[X^-]$ for the two anions are approximately linear [equation (4) where $(k_f^D)^{X^-}$ and $(k_f^D)^\circ$ are, respectively,

$$(k_f^D)^{X^-}/(k_f^D)^\circ = 1 + b^{X^-}[X^-] \qquad (4)$$

the first-order rate constants for deprotonation in the presence and absence of X^- (added as NaX and/or HX), and b^{X^-} is a constant characteristic of the anion]. Values of b^{Cl^-} and b^{ClO} (Table 5) are remarkably similar for the carbocations of the series (6c—f) and give calculated $(k_f^D)^{X^-}$ values [from equation (1)] in good agreement (within ±5%) with experimental values (*cf.* Tables 1 and 4; Figures 1 and 2) for the range of anion concentrations studied (0.1—0.4M).

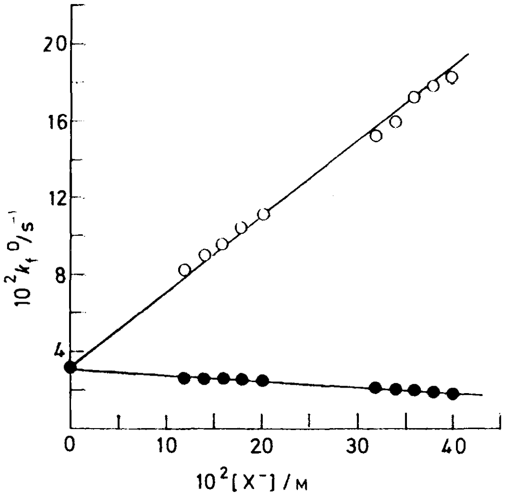


FIGURE 1 Variation in k_f^D for reactions of (6f) in H_2O–MeCN (1 : 1 w/w) at 25.0 °C in the presence of HX (0.12—0.20M) and of HX (0.12—0.20M) + NaX (0.20M): X = Cl (○) and X = ClO_4 (●)

Furthermore, these anion effects on rates of deprotonation are competitive; for reactions in acidic solutions containing both anions, the rate-enhancing effect of Cl^- is reduced by ClO_4^- (*cf.* k_f^D values; Table 4). This effect is illustrated in Figure 2 for reactions of (6e) and similar behaviour was found for the other carbocations (6c, d, and f). These results cannot be explained simply by the medium effects of the anions in solution, and they show that Cl^- and ClO_4^- must compete for the carbocations present. It follows that the cations (6) must be extensively ion-paired in aqueous acetonitrile but that only the (6)(Cl^-) pairs rapidly give alkene. The role of ion-pairing of intermediate carbocations in S_N1 solvolysis is well established,[14] but there is much less information concerning its effect in nucleophilic additions to preformed carbocations. The reduction in rates of additions to triarylmethyl[1b] and ferrocenylalkyl[5a] cations caused by the presence of salts of both inorganic and organic acids may be due, at least in part, to stabilisation of the carbocation by ion-pairing and to steric hindrance by the counter-ion to attack of the nucleophile. The potential effect of ion-pairing on rates of racemisation of chiral ferrocenylalkyl cations has been noted[15] but no investigation has been reported.

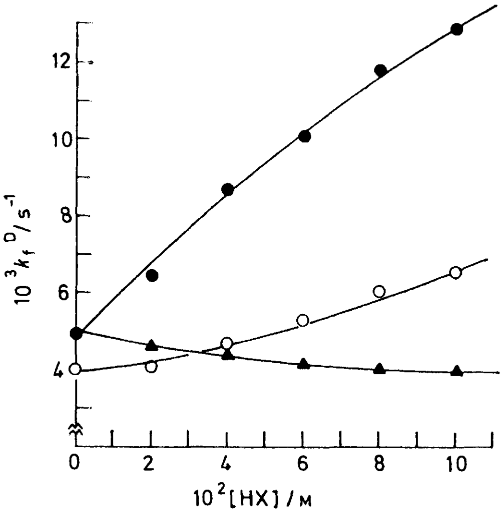


FIGURE 2 Variation in k_f^D values for reactions of (6e) at 25.0 °C in H_2O–MeCN (1 : 1 w/w) containing HCl (●), $HClO_4$ (▲), and HCl + 0.20M-$NaClO_4$ (○)

Because HCl is strong in aqueous acetonitrile,[16] Cl^- is not an external basic catalyst. However, Cl^- *in the ion-pair* may be sufficiently basic to assist proton loss from the carbocation. Such an effect has been proposed[3a] for concomitant S_N1-$E1$ reactions of tertiary alkyl substrates, where a higher proportion of elimination is found for reactions of halides than of related substrates with alternative leaving groups. Although complete studies were not carried out, we have found that Br^- also assists deprotonation of the cations (6e and f), but less effectively than Cl^-, and that deprotonation of the cation (6c) in methanol is retarded by $LiClO_4$, $NaClO_4$, and NaOTs, accelerated by LiCl, and strongly accelerated by NaOAc (which may be acting as a general base).

TABLE 5

Anion effects on rate constants for deprotonation of the cations (6d—f) in aqueous acetonitrile (1 : 1 w/w) [a]

Cation	R^1	R^2	$(k^D_f)^\circ/s^{-1}$	b^{Cl^-}/M^{-1} [b]	$b^{ClO_4^-}/M^{-1}$ [b]
(6c)	Ph	Bu^t	4.9×10^{-4}	15.4	−0.92
(6d)	Fc	H	1.0×10^{-2}	12.9	−1.3
(6e)	Fc	Me	4.9×10^{-3}	15.3	−0.90
(6f)	Fc	Ph	3.0×10^{-2}	13.4	−0.99

[a] At 25.0 °C. [b] Values refer to equation (4) (see text).

Conformational effects may also be important because ion-pairing may change the populations of the various conformations of the carbocations and thereby speed deprotonation, *e.g.* if the counter-ion in the ion-pair is preferentially located close to the formal C^+ centre above the *exo*-face of the pentafulvene-like ligand, conformer (8C) would be destabilised by steric repulsion between the anion and the β-substituent (R), leading to a preference for the ion-paired conformation (8A) which can undergo kinetically favoured *exo*-deprotonation with chloride assistance. In this hypothesis, we attribute the different effects upon deprotonation rates of carbocations paired with Cl^- and ClO_4^- to the disparate steric bulk of these anions; although both must pair with the cations, the much bulkier non-basic ClO_4^- may hinder loss of a proton, probably by excluding a water molecule from its vicinity, whereas the smaller Cl^- does not have this adverse effect.

Rates of Acid Heterolysis of Alcohols.—The transition states for acid heterolysis of 1-ferrocenylalkanols are carbocation-like, and the reaction occurs by a concerted process rather than by heterolysis of the conjugate acid of the alcohol formed by pre-equilibrium proton transfer.[5b,*] Rates (*cf.* k_r^A values; Table 2) of acid heterolysis of the alcohols (5) in H_2O–MeCN (1 : 1 w/w) increase through the series (5a) < (5c) < (5f) < (5e) < (5d). The faster reactions of the 1,1-diferrocenylalkanols (5d—f) compared with those of the 1-ferrocenyl-1-phenylalkanols (5a and c) therefore reflect the much greater stabilities (relative to the alcohols) of the 1,1-diferrocenylalkyl cations compared with those of 1-ferrocenyl-1-phenylalkyl analogues [the pK_{R^+} values for $Fc\overset{+}{C}HPh$ and $Fc_2\overset{+}{C}H$ in H_2O–MeCN (1 : 1 w/w) are −0.41 and 3.18, respectively [5a]].

There is no obvious correlation between the relative reactivities of the alcohols (5) towards acid heterolysis and those of the carbocations (6) towards water addition. Thus, although the least reactive alcohol (5a) of the series affords the most reactive carbocation (6a), the same order of reactivity is observed for the structurally related alcohols (5d—f) and the corresponding carbocations (6d—f), *i.e.* the most reactive alcohol (5d) affords the most reactive carbocation (6d) (*cf.* k_f^A and k_r^A values; Tables 1 and 2). Rates of acid heterolysis of 1-ferrocenylalkanols are known [5a] to be very sensitive to structural and conformational effects, which may account for the apparent irregularities.

For a given concentration of HCl or $HClO_4$, the alcohol (5e) undergoes heterolysis faster in 3 : 1 w/w H_2O–MeCN than in the less aqueous 1 : 1 w/w solvent (Table 2). The same effect has been noted [5a] for acid heterolysis of $(p\text{-}MeOC_6H_4)_3COH$ and other 1-ferrocenylalkanols in water and in H_2O–MeCN (1 : 1 w/w) and may reflect stabilisation of the alcohol by the organic solvent (*cf.* ref. 17). Heterolysis rates are also sensitive to the identity of the acid; the alcohols (5d—f) react faster with $HClO_4$ in aqueous acetonitrile than with HCl at the same molarity (Table 2). This effect is due to the different anions; acid heterolysis of 1-ferrocenylalkanols is accelerated by inorganic salts, with perchlorates more effective than chlorides.[5a] Similarly, rates of heterolysis of the less reactive alcohol (5c) in reactions with $HClO_4$ in aqueous acetonitrile are accelerated by addition of $NaClO_4$ (0.1M), but added NaCl (0.1M) has little effect on k_r^A (Table 3). Similar anion effects are observed in acid heterolyses of $(p\text{-}MeOC_6H_4)_3COH$.[1b,c]

Rates of Protonation of Alkenes.—Rates of protonation of the alkenes (7) are much more sensitive to structural effects than those of deprotonation of the resulting carbocations (6) (Table 4). The kinetic basicity increases through the series $(7a) \ll (7c) \ll (7f) \approx (7e) < (7d)$. Stabilisation of the carbon–carbon double bonds of the alkenes (7a and f) by conjugation of the β-phenyl group reduces their reactivities towards protonation, although the magnitude of the effect is probably attenuated by intramolecular repulsions which cause twisting of the phenyl and ferrocenyl groups from conformations in which resonance stabilisation is maximised; † in the crystal,[11] the planes of the C_5H_4 and *both* Ph rings of the *Z*-isomer of (7a) are twisted by *ca.* 45° from the double-bond plane. The relatively low reactivity of the alkene (7c) suggests steric hindrance by the bulky β-t-butyl group to proton transfer. To the extent that carbocation character has developed in the transition state for protonation, the higher reactivities of the 1,1-diferrocenylalkenes (7d—f) may be attributed to the additional stabilisation provided by the second ferrocenyl group.

Protonation of the alkenes (7e and f) in aqueous acetonitrile is modestly speeded by NaCl and $NaClO_4$ (Table 4), and increase in the water content of the solvent from 1 : 1 to 3 : 1 w/w H_2O–MeCN also speeds protonation of (7d) (*cf.* effects on k_r^A values, discussed earlier). These salt and solvent effects on protonation are readily understandable in that salts increase the protonating power of hydronium ions,[19] and an organic solvent reduces acidity by lowering the activity coefficient of the initial state relative to that of the hydronium ion and the transition state (*cf.* Table 2 in ref. 5a).

It is noteworthy that structural effects upon reactivities are similar for alkene protonation and acid heterolysis of alcohols [*i.e.*, rates of formation of the carbocations decrease through the series $(6d) > (6e) > (6f) > (6c) \gg (6a)$, for both reactions], and that both reactions show similar responses to acid, salt, and solvent effects. This suggests that the energies of the transition states for the two reactions are similarly influenced by structural change through the series and consequently that the transition state for protonation–deprotonation, like that for alcohol heterolysis–water addition,[5a] shows substantial carbocation character.

---

[*] The acid heterolysis of $Fc_2C(OH)Ph$ is general acid-catalysed (unpublished results).

[†] Conjugation of a carbon–carbon double bond with a ferrocenyl group confers slightly greater thermodynamic stability than that provided by a phenyl group.[18]

EXPERIMENTAL

For general remarks concerning synthetic methods, see ref. 20. Acetonitrile was purified as described previously.[5a] All new compounds gave satisfactory elemental analyses.

Preparation of Alcohols (5).—The alcohols were prepared from the corresponding ketones using existing procedures,[20] and were purified by chromatography (Al_2O_3). Additions of PhLi to $FcCOCH_2Ph$[21] and $FcCOCH_2Bu^t$[22] gave (5a), m.p. 103—105°, and (5c), m.p. 99—101°, respectively; additions of MeLi, EtMgBr, and $PhCH_2Li$[23] to Fc_2CO[24] gave (5d), m.p. 124—126°, (5e), m.p. 112—114°, and (5f), m.p. 130—132°, respectively. The ^1H n.m.r. spectra of these alcohols in $CDCl_3$ were as expected.

Preparation of Tetrafluoborates.—The BF_4^- salts of the cations (6a and c—f) were prepared from the corresponding alcohols by existing methods;[5a] the salt (6b) (BF_4^-) was prepared by the reaction of $FcC(Ph){=}CH_2$[25] and (Ph_3C^+)(BF_4^-) in dry alcohol-free CH_2Cl_2 and precipitation by dry Et_2O. Salts of (6a—c) are brown and those of (6d—f) are blue; these were stable in the dark in the absence of moisture in a refrigerator.

Preparation of Alkenes (7).—The alkenes (7a and c—f) were prepared by dehydration of the corresponding alcohols in acidified H_2O–MeCN, and the alkene (7b) by reaction of (6b) (BF_4^-) with NaOH in H_2O–MeCN, and were purified by chromatography (Al_2O_3). The ^1H n.m.r. spectra of the *E*- and *Z*-isomers of (7a), m.p. 118—120 and 105—107°, respectively, which were separated with some difficulty by repetitive t.l.c. (SiO_2), have been discussed.[11] The m.p.s and ^1H n.m.r. resonances (60 MHz; $CDCl_3$) of the other alkenes are as follows: (7b), m.p. 144—146°, τ 2.6—3.5 (21 H, m, Ph + vinyl) and 5.82—5.85 (9 H, s + s, Fc); (7c), m.p. 92—94°, τ 2.75 (5 H, s, Ph), 4.05 (1 H, s, vinyl), 6.0 (9 H, s, Fc), and 9.1 (9 H, s, Bu^t); (7d), m.p. 161—163° (lit.,[26] 162—164°), τ 4.53 (2 H, s, vinyl), 5.4 and 5.75 (8 H, 2t, C_5H_4), and 5.85 (10 H, s, C_5H_5); (7e), m.p. 152—154°, τ 5.45—5.55 (4 H, m), 5.7—5.9 (15 H, m + 2s) (Fc + vinyl), and 8.0 (3 H, d, Me); (7f), m.p. 108—110°, τ 2.7—2.9 (6 H) (s, Ph + vinyl), 5.05—5.15 (2 H), 5.65—5.85 (6 H, 2m, C_5H_4), and 5.85 and 6.0 (10 H, 2s, C_5H_5). The spectra of (7b and c) were consistent with the presence of a single stereoisomer in each case.

Rate Measurements.—Reactions with a half-life > *ca.* 1 s were followed using a Gilford spectrophotometer by mixing a solution (*ca.* 2 μl) of the alcohol (5), salt (6)(BF_4^-), or alkene (7) in MeCN, CH_2Cl_2 or $(CH_2Cl)_2$ with the reaction solution (*ca.* 3 ml; substrate concentration *ca.* 5×10^{-5}M) in a 1 cm cell at 25.0 °C and following the carbocation or alkene absorbance, as appropriate, at a suitable wavelength, *viz.* (6a), 340; (6b), 445; (6c), 338; (6d), 655; (6e), 720; (6f), 735; (7a), 307; (7c), 280 nm. At these wavelengths, absorption by the corresponding alcohol is negligible. The faster reactions [*i.e.* acid heterolysis of the alcohols (5d—f)] were followed at 25.0 °C using a Durrum–Gibson stopped-flow spectrophotometer by mixing a solution of the alcohol in H_2O–MeCN with an equal volume of the same solvent containing HCl or $HClO_4$ and following growth of carbocation absorbance at a suitable wavelength.

At least two separate determinations of each rate constant were carried out. Reactions were followed through at least three half-lives, and the first-order rate constants were calculated using a least-squares best-fit computer program; correlation coefficients >0.999 were obtained. The rate constants for the forward and reverse reactions (Scheme 2) were calculated as described in the Results section and are in Tables 1—4.

Determination of Product Ratios.—For reactions of (6a) (BF_4^-) with H_2O–MeCN, the kinetic product ratio [(7a)]/[(5a)] was determined by product isolation. A freshly prepared solution of the salt (200 mg) in MeCN (*ca.* 2 ml) was added to H_2O–MeCN (1 : 1 w/w) (*ca.* 100 ml) at 25.0 °C. The carbocation disappeared within 20 s and the solution was then neutralised (NaOH) and the products were thoroughly extracted (Et_2O) and cleanly separated by chromatography (Al_2O_3). Light petroleum eluted the alkene (7a) and light petroleum–Et_2O (20 : 1) eluted the alcohol (5a). The products were obtained almost quantitatively in the molar ratio [(7a)]/[(5a)] 0.50, in several determinations. Conversion of the alcohol into the alkene is negligible under these reaction conditions (*cf.* $t_{\frac{1}{2}}$ for alcohol heterolysis is *ca.* 29 min at [HBF_4] 4×10^{-3}M, the approximate final concentration of acid formed in the reaction), and the products are stable during chromatography on Al_2O_3. From reaction of (6b) (BF_4^-) with H_2O–MeCN, alkene (7b) was isolated almost quantitatively with no trace of the alcohol (5b).

The [alkene]/[alcohol] kinetic product ratios for reactions of the salts (6c—f)(BF_4^-) in H_2O–MeCN containing 10^{-3}M-4-picoline (to suppress alcohol heterolysis and alkene protonation), in the absence and presence of inorganic salts, were determined spectroscopically, under kinetic conditions, from relationship (5). The values $A_{R^+}{}^\circ$ and A_{R^+} are, respectively, the absorbances of carbocation (corrected for dilution, as necessary) corresponding to total product (alkene + alcohol) and to alcohol only for each solution, and A_∞ is the absorbance of alkene product at the same wavelength.

$$[\text{alkene}]/[\text{alcohol}] = \{A_R{}^\circ/(A_{R^+} - A_\infty)\} - 1 \qquad (5)$$

Because the alcohols (5c—f) do not absorb significantly at these wavelengths, A_∞ was obtained directly from the absorbance of the solutions after complete reaction of the carbocations. In all cases, wavelengths were chosen such that $A_\infty \ll A_{R^+}{}^\circ$.

Heterolysis of each of the alcohols (5c—f) is very much faster, at a given acidity, than either deprotonation of the resulting carbocations (6c—f) or protonation of the corresponding alkenes (7c—f) (*i.e.* $k_f{}^D \ll k_r{}^A[H^+] \gg k_r{}^D[H^+]$). Accordingly, for each solution of alkene + alcohol, predetermined acidification with H_2SO_4 rapidly (a few s) converted all the alcohol, but a negligible proportion of the alkene, into carbocation. Extrapolation of the slowly decaying (due to deprotonation) absorbance of the carbocation to the instant of acidification and correction for dilution gave the appropriate A_{R^+} value for the solution.

Because the reaction of (6c) (BF_4^-) with H_2O–MeCN is relatively slow ($t_{\frac{1}{2}}$ *ca.* 14.5 min), $A_{R^+}{}^\circ$ for the mixture of (5c) + (7c) was obtained by extrapolation of the carbocation absorption to zero reaction time following addition of (6c) (BF_4^-) to the reaction medium. For the more reactive cations (6d—f), values of $A_{R^+}{}^\circ$ were determined from the carbocation absorbances following addition to the solutions of products of sufficient 5.0M-H_2SO_4 to convert all the alcohol and all (or a predetermined proportion > 90%) the alkene into carbocation, and correcting for dilution.

These kinetic product ratios were reproducible in several determinations.

Determination of Carbocation : Alkene Equilibrium Ratios.—For a given [HCl] or [$HClO_4$] in H_2O–MeCN, the [carbocation]/[alkene] equilibrium molar ratios for the systems (6d—f) : (7d—f) were determined from relationship (6)

$$([R^+]/[\text{ene}])_{eq} = A_{R^+}/(A_{R^+}{}^\circ - A_{R^+}) \qquad (6)$$

where A_{R^+} and $A_{R^+}{}^\circ$ are, respectively, the absorbances of carbocation present in solution of a particular [H$^+$], and of carbocation corresponding to total substrate (carbocation + alkene). Analyses were carried out at wavelengths >650 nm where alkene absorption is negligible.

Values of $A_{R^+}{}^\circ$ and A_{R^+} were determined as follows. Exactly 12 μl of a stock solution (*ca.* 1.2×10^{-2}M) of alcohol (5d—f) in $(CH_2Cl)_2$ was mixed thoroughly with 3.0 ml of acidic solvent in a 1 cm cell at 25.0 °C and the carbocation absorbance was immediately monitored. Extrapolation of this falling absorbance (due to deprotonation) to time of mixing gave the $A_{R^+}{}^\circ$ value because, at the [H$^+$] used, the alcohols are rapidly and quantitatively converted into carbocation. The corresponding A_{R^+} value was then obtained from the carbocation absorption when equilibrium had been established. The alcohol concentration in these solutions is negligible. Several determinations were made for each [H$^+$] and the results agreed.

The procedure was modified slightly for determination of the equilibrium ratios [(6c)]/[(7c)] because the alkene (7c) absorbs, although weakly, at the wavelength (338 nm) of analysis. The equilibrium absorbance was recorded as before following addition of a portion of a stock solution of alkene (7c) to the acidic solvent, and the percentage carbocation was determined from this value and those for equimolar solutions containing no acid (100% alkene) and concentrated acid (100% carbocation), using the Beer–Lambert law. Duplicate determinations agreed.

Support of this work by the National Science Foundation, the Petroleum Research Fund administered by the American Chemical Society, and the S.R.C. is gratefully acknowledged. N. Carrasco was on leave from the Universidad Técnica del Estado, Santiago, Chile. W. E. W. thanks the Leverhulme Trust for a Research Fellowship. N. Cully thanks the Northern Ireland Department of Education for a postgraduate grant.

[0/723 *Received*, 16*th May*, 1980]

REFERENCES

[1] (*a*) C. D. Ritchie, *Accounts Chem. Res.*, 1972, **5**, 348; *Pure Appl. Chem.*, 1978, **50**, 1281, and references cited therein; (*b*) C. A. Bunton and S. K. Huang, *J. Amer. Chem. Soc.*, 1972, **94**, 3536; 1973, **95**, 2701; 1974, **96**, 515; C. A. Bunton, S. K. Huang, and C. H. Paik, *ibid.*, 1975, **97**, 6262; (*c*) M. J. Postle and P. A. H. Wyatt, *J.C.S. Perkin II*, 1972, 474; J. N. Ride and P. A. H. Wyatt, *ibid.*, 1973, 746.

[2] See D. V. Banthorpe, 'Elimination Reactions,' Elsevier, Amsterdam, 1963; W. H. Saunders and A. F. Cockerill, 'Mechanisms of Elimination Reactions,' Wiley–Interscience, New York, 1973.

[3] (*a*) M. Cocivera and S. Winstein, *J. Amer. Chem. Soc.*, 1963, **85**, 1702; (*b*) C. A. Bunton, T. W. Del Pesco, A. M. Dunlop, and K.-U. Yang, *J. Org. Chem.*, 1971, **36**, 887; (*c*) J. F. Bunnett and D. L. Eck, *ibid.*, p. 897.

[4] See W. E. Watts, *J. Organometallic Chem. Library*, 1979, **7**, 399.

[5] (*a*) C. A. Bunton, N. Carrasco, and W. E. Watts, *J.C.S. Perkin II*, 1979, 1267; (*b*) C. A. Bunton, N. Carrasco, F. Davoudzadeh, and W. E. Watts, *ibid.*, 1980, 1520.

[6] C. A. Bunton, W. Crawford, N. Cully, and W. E. Watts, *J.C.S. Perkin I*, 1980, 2213; W. Crawford and W. E. Watts, *J. Organometallic Chem.*, 1980, **185**, 443.

[7] A. P. G. Kieboom, *Chem. and Ind.*, 1978, 434; see also S.-C. Chen and R. M. Elofson, *ibid.*, p. 64; B. Floris, *J. Org. Chem.*, 1976, **41**, 2774; S.-C. Chen, C. C. Lee, and R. G. Sutherland, *Synth. React. Inorg. Metal-org .Chem.*, 1977, **7**, 565.

[8] *Cf.* W. M. Horspool, R. G. Sutherland, and J. R. Sutton, *Canad. J. Chem.*, 1970, **48**, 3542; W. M. Horspool, P. Stanley, R. G. Sutherland, and B. J. Thomson, *J. Chem. Soc.* (*C*), 1971, 1365; W. M. Horspool, R. G. Sutherland, and B. J. Thomson *Synth. React. Inorg. Metal-org. Chem.*, 1972, **2**, 129.

[9] Preliminary communications, C. A. Bunton and W. E. Watts, *Tetrahedron Letters*, 1977, 2049; C. A. Bunton, N. Carrasco, and W. E. Watts, *ibid.*, 1980, 407.

[10] C. A. Bunton, N. Carrasco, and W. E. Watts, unpublished results.

[11] C. J. Cardin, W. Crawford, W. E. Watts, and B. J. Hathaway, *J.C.S. Dalton*, 1979, 970.

[12] T. S. Abram and W. E. Watts, *J.C.S. Perkin I*, 1977, 1522.

[13] Z. Rappoport, *Tetrahedron Letters*, 1979, 2559.

[14] See S. R. Hartshorn, 'Aliphatic Nucleophilic Substitution,' Cambridge University Press, London, 1973, ch. 4; J. M. Harris, *Progr. Phys. Org. Chem.*, 1974, **11**, 89.

[15] S. Allenmark, K. Kalén, and A. Sandblom, *Chem. Scripta*, 1975, **7**, 97.

[16] C. Moreau and G. Douhéret, *J. Chim. Phys.*, 1974, **71**, 1313.

[17] See F. A. Long and M. A. Paul, *Chem. Rev.*, 1957, **57**, 935.

[18] A. M. Easton, M. J. A. Habib, J. Park, and W. E. Watts, *J.C.S. Perkin II*, 1972, 2290.

[19] See R. H. Boyd in 'Solute–Solvent Interactions,' eds. J. F. Coetzee and C. D. Ritchie, Marcel Dekker, New York, 1969, ch. 3.

[20] T. D. Turbitt and W. E. Watts, *J.C.S. Perkin II*, 1974, 177.

[21] N. Sugiyama, H. Suzuki, Y. Shioura, and T. Teitei, *Bull. Chem. Soc. Japan*, 1962, **35**, 767.

[22] T. S. Abram, T. D. Turbitt, and W. E. Watts, *J.C.S. Perkin I*, 1977, 1536.

[23] H. Gilman and H. A. Ninch, *J. Org. Chem.*, 1961, **26**, 3723.

[24] P. L. Pauson and W. E. Watts, *J. Chem. Soc.*, 1962, 3880.

[25] K.-L. Wu, E. B. Sokolova, L. A. Leites, and A. D. Petrov, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1962, 887.

[26] K. L. Rinehart, P. A. Kittle, and A. F. Ellis *J. Amer. Chem Soc.*, 1960, **82**, 2082.