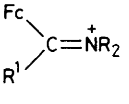
# A Kinetic Study of the Hydrolysis of Ferrocenyliminium Ions

**Clifford A. Bunton, Faegh Davoudzadeh, and Mansingrao H. Jagdale**
*Department of Chemistry, University of California, Santa Barbara, California 93106, U.S.A.*
**William E. Watts ***
*School of Physical Sciences, New University of Ulster, Coleraine, Northern Ireland BT52 1SA*

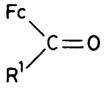
Rate constants have been determined for reaction of $PF_6^-$ salts of ferrocenyliminium ions $FcC(R^1)=\overset{+}{N}R_2$ (1) and $FcC(R^1)=\overset{+}{N}HR$ (3) (Fc = ferrocenyl; $R^1$ = H, Me, or aryl; R = H or alkyl) with hydroxide ion in water and in $H_2O$–MeCN (1 : 1 w/w). The reactions, which are faster in the mixed solvent, give acylferrocenes quantitatively and proceed by rate-limiting nucleophilic addition to the iminium ions. Increasing bulk of groups attached to the $C=\overset{+}{N}$ system retards reaction, with a much larger steric effect exerted by *C*-substituents than by $\overset{+}{N}$-substituents. Electronic effects of substituents on rates are relatively small. Reaction is very slow in the absence of added hydroxide ion and is not catalysed by general bases, and the reactivity of water relative to that of hydroxide ion towards the iminium ions is much lower than predicted by the $N_+$ nucleophilicity scale. Added inorganic salts retard reaction. The reactivities of the ions (1) and (3) towards water and hydroxide ion are lower than those of aryl analogues, and the ions (3) are slightly weaker acids than protonated imines derived from substituted benzaldehydes and benzophenones.

Reactions of imines and iminium ions are important in chemical and biochemical systems.[1] Rates of formation and hydrolysis of imines derived from aromatic aldehydes or ketones and primary aromatic[2] or aliphatic[3-5] amines have been thoroughly investigated. Protonated imines of the types $ArCH=\overset{+}{N}HR$ and $Ar_2C=\overset{+}{N}HR$ are accessible in solution as reaction intermediates and rate and equilibrium constants for some of the steps in their hydrolysis have been estimated,[3,4] but there has been relatively little kinetic study of reactions of pre-formed iminium ions.

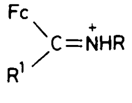
The ferrocenyl group (Fc) is very strongly electron-donating[6] and rates of nucleophilic addition and deprotonation of preformed ferrocenylalkylium ions can be conveniently followed.[7] Salts of ferrocenyliminium ions have been synthesised[8,9] and we now report a kinetic study of reactions of the ions (1) and (3) and the related imines (4) in aqueous solution. The spectroscopic properties[9a] of all the salts used and the crystal structure[10] of a representative example, *viz.* (1a) $[PF_6^-]$, are more in accord with an iminium structure $(C=\overset{+}{N})$ than an amino-carbocation formulation $(\overset{+}{C}-\dot{N})$.



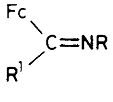
(1)



(2)



(3)

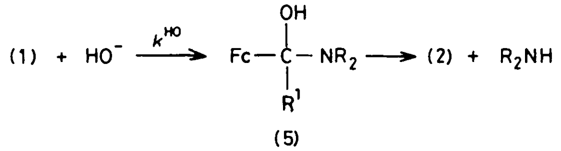


(4)

(1):
a; $R^1$ = H, R = Me
b; $R^1$ = H, R = Et
c; $R^1$ = H, R = $Pr^i$
d; $R^1$ = Ph, R = Me
e; $R^1$ = Ph, R = Et
f; $R^1$ = Mp, R = Me

(3):
a; $R^1$ = H, R = Me
b; $R^1$ = H, R = $Bu^t$
c; $R^1$ = R = Me
d; $R^1$ = Ph, R = H
e; $R^1$ = Ph, R = Me
f; $R^1$ = Mp, R = H

(Fc = ferrocenyl, Mp = *p*-methoxyphenyl)



(5)

Scheme 1.

## Results

*Hydrolysis of* N,N-*Dialkyliminium Ions.*—The iminium ions (1a—f) react readily with NaOH in water or $H_2O$–MeCN (1 : 1 w/w) giving the corresponding acylferrocenes (2) and secondary amines quantitatively.[9b] These reactions probably involve intermediate α-hydroxy-amines (5) (Scheme 1) but these were not detected and, so far as we know, have only transient existence, so that the rate-limiting step is probably addition of $HO^-$ to the iminium ion. The rates of reactions were followed spectrophotometrically (see Experimental section) and were first-order in $[HO^-]$; the second-order rate constants ($k^{HO}$) are in Table 1.

Hydrolysis of these iminium ions was also followed in unbuffered water (pH *ca.* 6) and in unbuffered $H_2O$–MeCN (pH *ca.* 7.7). These reactions are very slow and, in some cases, reaction with $HO^-$ (from the autoprotolysis of water) makes a major contribution to the observed rate constant ($k_\psi$). We corrected for reaction with $HO^-$ using equation (i) and

$$k_\psi = k^{HO}[HO^-] + k^{H_2O} \qquad (i)$$

calculating $[HO^-]$ from the measured pH of the solution. This correction is only approximate, but it is obvious that water is a very poor nucleophile towards these iminium ions. Two experiments in unbuffered, slightly acidic water gave values of $k^{H_2O}$ similar to those estimated at pH *ca.* 6. Values of $k_\psi$ and $k^{H_2O}$ are in Table 1. Reactions of the ions (1d—f) with water are so slow that we did not estimate rate constants.

*Buffer and Salt Effects on Rates.*—Hydrolysis of the ion (1a) in water is not catalysed by acetate or carbonate buffers (Table 2). The small rate changes observed are probably due to specific salt effects. As expected, added inorganic salts inhibit attack of $HO^-$ on the iminium ions (1d and e) (Table 3). Most experiments were carried out with not more than $10^{-2}$M-NaOH in water, but with NaCl and $NaClO_4$ we varied $[HO^-]$ between $10^{-2}$ and $10^{-1}$M; the salt concentrations were 0.1 and 0.5M.

*Hydrolysis of* N-*Protonated Iminium Ions.*—Addition of an excess of NaOH to aqueous solutions of the iminium ions

**Table 1.** Rate constants for reactions of *N*,*N*-dialkyliminium ions[a]

| | Reaction in $H_2O$ | | | Reaction in $H_2O$–MeCN[b] | |
|---|---|---|---|---|---|
| Cation | $k^{HO}$ | $10^5k_\psi$ | $10^5k^{H_2O}$ | $k^{HO}$ | $10^5k_\psi$ |
| $FcCH{=}\overset{+}{N}Me_2$ (1a) | $3.33 \times 10^3$ | 7 | 4[c] | $2.06 \times 10^4$ | 17 |
| $FcCH{=}\overset{+}{N}Et_2$ (1b) | $9.90 \times 10^2$ | 1.2 | 0.2 | | |
| $FcCH{=}\overset{+}{N}Pr^i_2$ (1c) | $2.18 \times 10^2$ | | | $1.37 \times 10^2$ | 9 |
| $FcC(Ph){=}\overset{+}{N}Me_2$ (1d) | 26.7 | *ca.* 0 | | $1.30 \times 10^2$ | *ca.* 0 |
| $FcC(Ph){=}\overset{+}{N}Et_2$ (1e) | 4.05 | *ca.* 0 | | 21.1 | *ca.* 0 |
| $FcC(Mp){=}\overset{+}{N}Me_2$ (1f) | 22.2 | *ca.* 0 | | 85.0 | *ca.* 0 |

[a] At 25.0 °C; $k^{HO}$ in l mol$^{-1}$ s$^{-1}$ is the second-order rate constant for reaction with $HO^-$, $k_\psi$ in s$^{-1}$ is the observed first-order rate constant for reaction in the absence of added $HO^-$, and $k^{H_2O}$ in s$^{-1}$ is the estimated (see text) first-order rate constant for reaction with $H_2O$. [b] 1 : 1 w/w, [c] For reactions in water at pH 4.5 and 5.5 (unbuffered), $10^5k_\psi = 4.2$ and 5.3 s$^{-1}$, respectively, corresponding to $10^5k^{H_2O}$ = *ca.* 4 s$^{-1}$.

**Table 2.** Reactions of iminium ion (1a) in buffers[a]

| Buffer | | |
|---|---|---|
| Acetate[b] | Carbonate[c] | $10^5k_\psi$/s$^{-1}$ |
| 0.08 | | 6.13 |
| 0.16 | | 6.05 |
| 0.24 | | 6.15 |
| | 0.03 | 242 |
| | 0.05 | 223 |
| | 0.07 | 235 |
| | 0.10 | 286 |
| | 0.15 | 250 |
| | 0.10 | 886[d] |
| | 0.15 | 702[d] |
| | 0.20 | 577[d] |

[a] In water at 25.0 °C with 1.0M-NaCl unless otherwise specified. [b] Molarity of NaOAc; $[AcO^-]/[HOAc] = 1.25$. [c] Molarity of $Na_2CO_3$; $[CO_3^{2-}]/[HCO_3^-] = 1.0$. [d] In the absence of NaCl.

**Table 3.** Second-order rate constants ($k^{HO}$) for reactions with hydroxide ion in the presence of salts[a]

| | Iminium ion | |
|---|---|---|
| Salt | $FcC(Ph){=}\overset{+}{N}Me_2$ (1d) | $FcC(Ph){=}\overset{+}{N}Et_2$ (1e) |
| None | 26.7 | 4.05 |
| LiCl | | 2.90 (1.93) |
| NaCl[b] | 17.5 (11.8) | 2.82 (1.71) |
| NaBr | | 2.59 (1.71) |
| $NaNO_3$ | 17.0 (9.4) | 2.43 (1.57) |
| $NaClO_4$[b] | 14.5 (7.3) | 2.35 (1.05) |
| NaOTs | | 2.42 (1.05) |
| $Me_4NBr$ | | 3.49 (2.45) |
| $Me_4NNO_3$ | | 2.91 (2.16) |

[a] In l mol$^{-1}$ s$^{-1}$ at 25.0 °C in water with $10^{-2}$M-NaOH, unless otherwise specified, and 0.1M-salt; values in parentheses are for 0.5M-salt. [b] From rate constants with $10^{-2}$—$10^{-1}$M-NaOH.

(3a—f) causes an immediate loss of the absorbance characteristic of the iminium ion which is quantitatively deprotonated to the imine; the latter is inert to $HO^-$ under these conditions. These imines (4a—f) have been isolated and their structures confirmed by $^1H$ n.m.r. spectroscopy.[9a] No evidence was found for the presence of isomers $FcCH(R^1)N{=}CH_2$ of the *N*-methyl compounds (4a, c, and e); earlier work[11] has shown that conjugation of a double bond with a ferrocenyl group confers at least as much stabilisation as that provided by an aryl group.

However, if reactions are carried out at lower pH, such that the iminium ion and imine are present in equilibrium, then hydrolysis to acylferrocene proceeds to completion (Scheme 2). For this system, the variation in the observed rate constant ($k_\psi$) with $[HO^-]$ can be expressed as in equation (ii). Reactions

$$k_\psi = k^{HO}K_b[HO^-]/(K_b + [HO^-]) \qquad \text{(ii)}$$

$$\text{or } 1/k_\psi = 1/k^{HO}[HO^-] + 1/k^{HO}K_b \qquad \text{(iia)}$$

were followed in carbonate buffers, ionic strength 0.1M, and $[HO^-]$ was calculated from the measured pH of the solution. Plots of $1/k_\psi$ against $1/[HO^-]$ were linear, *cf.* equation (iia), and $k^{HO}$ and $K_b$ were calculated from the slope and intercept, based on a least-squares calculation. Typical plots are given in Figures 1 and 2 in the Supplementary Publication.* Values of $k^{HO}$ and $pK_a$ (from $K_a = 1/K_b$) are in Table 4.

$$(4) + H^+ \underset{}{\overset{K_b}{\rightleftharpoons}} (3) \xrightarrow[HO^-]{k^{HO}} (2) + RNH_2$$

**Scheme 2.**

We also examined reactions of some of these ions in unbuffered water at pH *ca.* 6, where there should be little deprotonation of the iminium ion. Generally, these reactions are very slow but for (3a), $k_\psi = 2.6 \times 10^{-4}$ s$^{-1}$. At this pH, the contribution of the reaction with $HO^-$ should have been *ca.* $1.9 \times 10^{-4}$ s$^{-1}$, which gives a rate constant for the water reaction $k^{H_2O}$ = *ca.* $7 \times 10^{-5}$ s$^{-1}$. However, this estimate is subject to large uncertainty because the experiment was conducted in an unbuffered solution. With the other ions (3b—f), we saw no evidence for a water reaction.

## Discussion

*Solvent Effects.*—For those substrates for which direct comparison can be made, the rate constants ($k^{HO}$) for reactions of ferrocenyliminium ions with $HO^-$ in $H_2O$–MeCN (1 : 1 w/w) are 4—6 times larger than corresponding values in water (Table 1). This effect is more pronounced than that found previously for additions of $HO^-$ and other anionic nucleophiles to ferrocenylalkylium ions; *e.g.* the second-order rate constants for $HO^-$ addition to $Fc\overset{+}{C}HMp$ and $Fc_2\overset{+}{C}H$ in $H_2O$–MeCN (1 : 1 w/w) are, respectively, *ca.* 1.2 and 1.7 times those for reactions in water.[7b] The higher reactivity of $HO^-$ in the mixed solvent may arise because the nucleophile is less

---

* Supplementary Publication No. SUP 23807 (5 pp.). For details of Supplementary Publications see Instructions for Authors, *J. Chem. Soc., Perkin Trans. 2*, 1984, Issue 1.

**Table 4.** Reactions of protonated imines [a]

| Cation | $pK_a$ | $k^{HO}$/ l mol$^{-1}$ s$^{-1}$ | $k_\psi$/s$^{-1}$ [b] |
|---|---|---|---|
| $FcCH{=}\overset{+}{N}HMe$ (3a) | 8.5 | $1.91 \times 10^4$ | $2.6 \times 10^{-4}$ |
| $FcCH{=}\overset{+}{N}HBu^t$ (3b) | 8.8 | $9.90 \times 10^3$ | $3 \times 10^{-5}$ |
| $FcC(Me){=}\overset{+}{N}HMe$ (3c) | *ca.* 9.5 | $2.80 \times 10^2$ | *ca.* 0 |
| $FcC(Ph){=}\overset{+}{N}H_2$ (3d) | 8.0 | $1.95 \times 10^2$ | *ca.* 0 |
| $FcC(Ph){=}\overset{+}{N}HMe$ (3e) | 7.9 | $1.55 \times 10^2$ | *ca.* 0 |
| $FcC(Mp){=}\overset{+}{N}H_2$ (3f) | 8.0 | $1.67 \times 10^2$ | *ca.* 0 |

[a] In water at 25.0 °C with carbonate buffer, ionic strength 0.1M (NaCl), unless otherwise specified. [b] Observed first-order rate constants for reactions in unbuffered water at pH *ca.* 6, not corrected for the contribution of reaction with $HO^-$.

effectively solvated than in water alone. It has been argued[12] that activation barriers to additions of anions to carbocations in aqueous solution arise predominantly from the energy required for desolvation of the nucleophile.

*Effect of Structure on Reactivity*.—Substituents $R^1$ and R in the iminium ions may exert steric and electronic effects on reactivity. At first sight, electronic effects seem to be small; *e.g.* replacement of a phenyl group at the reaction centre [(1d) and (3d)] by a *p*-methoxyphenyl (Mp) group [(1f) and (3f)] only slightly inhibits reaction with $HO^-$ (Tables 1 and 4). This observation is consistent with an iminium bond order close to two, with most of the positive charge on nitrogen, as concluded earlier.[9,10]

However, analysis of electronic effects of aryl groups in such systems is complicated by steric interactions between the ferrocenyl and aryl groups attached to the reaction centre which cause the latter to twist out of the plane of the attached $sp^2$-hybridised carbon; *cf.* crystal structure of (*Z*)-FcC(Ph)=CHPh.[13] This twisting reduces mesomeric electron donation by the aryl group, such that its $-I$ effect gains in relative importance, and also increases steric hindrance to nucleophilic addition. The importance of this torsional effect can be seen by comparing the effects of $\overset{+}{C}$-aryl groups upon the properties of benzylic and ferrocenylmethyl cations; *e.g.* much larger differences in stability and electrophilic reactivity are found through the series $Mp\overset{+}{C}Ph_2$, $Mp_2\overset{+}{C}Ph$, $Mp_3\overset{+}{C}$ than for the series $Fc\overset{+}{C}Ph_2$, $Fc\overset{+}{C}(Ph)Mp$, $Fc\overset{+}{C}Mp_2$.[7a,14]

Not surprisingly, steric effects on reactivity are more important at carbon, the reaction site, than at nitrogen of the $C{=}\overset{+}{N}$ system; *e.g.* $FcCH{=}\overset{+}{N}HMe$ (3a) is *ca.* 70 times more reactive towards $HO^-$ than is $FcC(Me){=}\overset{+}{N}HMe$ (3c) (Table 4). A similar effect has been found for equilibrium hydration of aldehydes and ketones.[15] On the other hand, the relative reactivities of $FcCH{=}\overset{+}{N}Me_2$, $FcCH{=}\overset{+}{N}Et_2$, and $FcCH{=}\overset{+}{N}Pr^i_2$ (1a—c) towards $HO^-$ in water are *ca.* 15 : 5 : 1, respectively (Table 1), and replacement of the methyl group of $FcCH{=}\overset{+}{N}HMe$ (3a) by a t-butyl group (3b) only halves the reactivity (Table 4).

The *N*-protonated imines (3) are more reactive towards $HO^-$ than the corresponding *N*,*N*-dialkyliminium ions (1) (Tables 1 and 4),* probably for steric reasons. There may also be a difference between the two systems because of changes in hydrogen-bonding between a protonated imine and solvent water on addition of $HO^-$ to (3). However, this change in solvation does not seem to be of major importance because (3d) and (3e) have similar reactivities towards $HO^-$, although we note the possibility of co-existence of *E*- and *Z*-isomers of some of the ions (3),† so that some of the rate and equilibrium constants in Table 4 are apparent values.

The ferrocenyliminium ions (1) and (3) are much less reactive towards water and $HO^-$ than related ferrocenylalkylium ions, as expected if the positive charge in the former is largely on nitrogen; *e.g.* the relative reactivities towards $HO^-$ in water of $Fc\overset{+}{C}HMp$, $FcC(Mp){=}\overset{+}{N}H_2$, and $FcC(Mp){=}\overset{+}{N}Me_2$ are *ca.* 1 670 : 8 : 1, respectively (ref. 7*b* and Tables 1 and 4).

*General Base and Salt Effects*.—Addition of water to preformed carbocations (*e.g.* $Mp_3\overset{+}{C}$) is general base-catalysed,[16] and general acid catalysis of the reverse reaction has been observed for heterolyses of tropyl alcohol and $Fc_2C(OH)Ph$.[7e] General base catalysis was not observed in water addition to ferrocenyliminium ions, and the variations of $k_\psi$ with [buffer] which we observe (Table 2) are probably due to specific salt effects. Attack of water on $Ph_2C{=}\overset{+}{N}Me_2$ is catalysed by carboxylate ions with a Brønsted β-coefficient of 0.27,[3b] and if β for reactions of the ferrocenyliminium ions is close to zero, a minor base-catalysed contribution to reaction could have been obscured by the specific electrolyte effects. In addition, it is difficult to separate rate contributions of reaction with $HO^-$ from those of general base catalysis. For reactions of aryliminium ions in which nucleophilic addition is rate-limiting, $HO^-$ acting as a nucleophile is a better catalyst than predicted by a linear Brønsted plot,[3b] consistent with general base catalysis being relatively unimportant in hydrolyses of ferrocenyliminium ions.

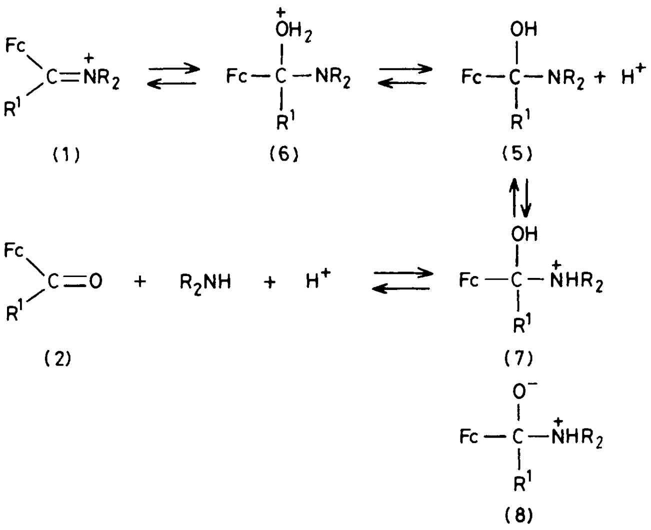
Addition of $HO^-$ to ferrocenyliminium ions is inhibited by added inorganic salts (Table 3), and these salt effects are qualitatively similar to those observed earlier for attack of water and $HO^-$ upon $Ar_3\overset{+}{C}$[14] and ferrocenylalkylium ions.[7a] As with these carbocation reactions, inhibition increases with increasing anion bulk and decreasing charge density (*cf.* effects of added chloride, tosylate, and perchlorate salts), but specificity appears to be more pronounced for reactions of the carbocations than of the iminium ions. Whereas water addition to $Fc\overset{+}{C}HMp$ is modestly accelerated in the presence of $Me_4NCl$,[7a] nucleophilic addition to the ferrocenyliminium ions (and also to $Mp_3\overset{+}{C}$[14]) is inhibited by $Me_4\overset{+}{N}$ salts, albeit to a smaller extent than that caused by corresponding $Na^+$ salts. These ion specificities could be related to the ability of the anions to pair with the reacting cations, to the relative hydrophobicity of $Me_4\overset{+}{N}$, and to the effect of salt ions on the hydrogen-bonding properties of water. A detailed discussion of salt effects in nucleophilic additions to carbocations has been given.[14]

*Comparison of Reactivities of Ferrocenyl- and Aryl-iminium Ions*.—Earlier work[3—5] has shown that the reactivities towards water and $HO^-$ of iminium ions derived from benzaldehyde or benzophenone and aliphatic amines are increased by electron-withdrawing and reduced by electron-donating *p*-substituents; *e.g.* the relative rates of $HO^-$ addition to

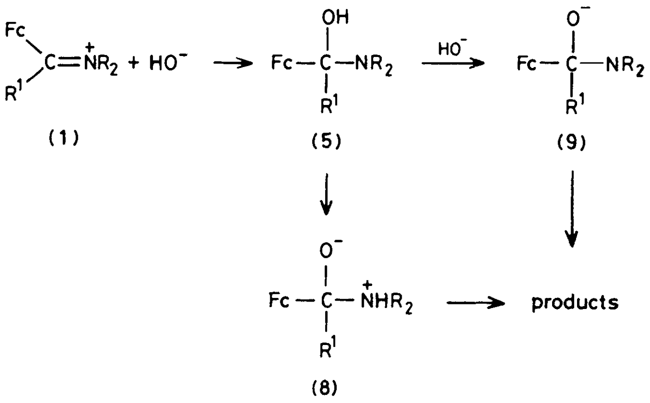
---

* Rates of reactions of the protonated imines (3) with $HO^-$ were subject to a small negative salt effect of carbonate buffer plus NaCl (see Experimental section).

† Spectroscopic studies[9a] have established an *E* stereochemistry for the iminium ions (3a and b) and shown that the iminium ion (3e) is a mixture of *E*- and *Z*-isomers.



Scheme 3.



Scheme 4.

ArCH=$\overset{+}{\mathrm{N}}$HBu$^t$ for Ar = Ph, *p*-nitrophenyl, and *p*-methoxyphenyl are *ca.* 1 : 6.4 : 0.1, respectively.[3a] Given that the electron-donating ability of the ferrocenyl group vastly exceeds that of aryl groups including Mp,[6] it is unsurprising that ferrocenyliminium ions are hydrolysed less readily than aryl analogues. For example, comparison of second-order rate constants for HO$^-$ addition in water (ref. 3 and Tables 1, 4) shows that Ph$_2$C=$\overset{+}{\mathrm{N}}$H$_2$ is *ca.* 5 times more reactive than FcC(Ph)=$\overset{+}{\mathrm{N}}$H$_2$, MpC(Ph)=$\overset{+}{\mathrm{N}}$Me$_2$ is *ca.* 11 times more reactive than FcC(Ph)=$\overset{+}{\mathrm{N}}$Me$_2$, and MpCH=$\overset{+}{\mathrm{N}}$HBu$^t$ is *ca.* 5 times more reactive than FcCH=$\overset{+}{\mathrm{N}}$HBu$^t$. These comparisons undervalue the reactivity differences to some extent because the rate constants for the aryliminium ions, but not the ferrocenyl analogues, were determined in the presence of 0.5M-KCl which would inhibit reaction by a kinetic salt effect (*cf.* Table 3). However, the reactivity differences between aryl and ferrocenyl substrates are not large, and presumably arise mainly from the difference in electronic properties although steric and conformational effects may also contribute.

*Relative Nucleophilicities of Water and Hydroxide Ion.*—Water is an ineffective nucleophile towards ferrocenyliminium ions (Table 1). The contribution of its reaction is too small to be detected with most of the substrates, and even where we appear to see a water reaction, its contribution is almost within the limits of uncertainty. This behaviour is somewhat unusual; *e.g.* water is an effective nucleophile in additions to a variety of preformed carbocations, including ferrocenylalkylium ions, and in deacylations. Based on the limited data available, our estimate of the relative reactivities ($k^{\mathrm{HO}}/k^{\mathrm{H_2O}}$) of HO$^-$ and water towards ferrocenyliminium ions is *ca.* $10^8$ (Table 1), whereas relative reactivities based on the $N_+$ scale[12] and the Swain–Scott scale[17] are *ca.* $6 \times 10^4$ and $2 \times 10^4$, respectively. These estimates are electrophile-dependent, but not to an extent which invalidates our general conclusion regarding the unreactivity of ferrocenyliminium ions towards water. This difference in reactivity of HO$^-$ and water is similar to, but somewhat larger than, those observed earlier for attack upon protonated arylimines[3] for which $k^{\mathrm{HO}}/k^{\mathrm{H_2O}}$ values range from *ca.* $7 \times 10^5$ for Ph$_2$C=$\overset{+}{\mathrm{N}}$H$_2$ to *ca.* $10^8$ for MpCH=$\overset{+}{\mathrm{N}}$HBu$^t$.

In a multi-step reaction (*e.g.* as in Scheme 3), the initial water addition may be much faster than the overall reaction because of return of intermediate(s) to reactants; for example, the presumed intermediate α-hydroxy-amine (5), which apparently has a short lifetime, may partition unfavourably. We see no general base catalysis of the water reaction, suggesting that the initial reaction gives a cationic intermediate (6) which should go rapidly to (5) and, at pH 6, (5) should then give (7). Alternatively, (6) may go directly to (7). At this pH, return of (7) to (5) or (6) should be relatively unfavourable, so that (7) should go forward to products, possibly *via* the zwitterion (8).* Similar arguments apply if (5) is formed directly from (1) in a general base-catalysed reaction with a low value of β.

It seems unlikely, therefore, that the low reactivity of water as compared with HO$^-$ can be due to unfavourable partitioning of the intermediate (5). We conclude that, for reactions of ferrocenyliminium ions and also iminium ions derived from benzaldehydes and benzophenones,[3] the reactivity of water relative to HO$^-$ is much lower than predicted by the $N_+$ relative nucleophilicity scale, even though this scale can be applied successfully to a variety of reactions that involve rate-limiting nucleophilic additions to *sp*$^2$-hybridised carbon atoms.[12]

Reaction pathways at high pH are shown in Scheme 4. The first-formed intermediate (5) could go forward to products either *via* the zwitterion (8) involving proton transfer, or the anion (9) involving deprotonation. If (9) is on the reaction path to products, its formation must be rapid relative to return of (5) to reactants because the reaction rates are no more than first-order in [HO$^-$]. Either pathway seems reasonable and we see no simple way of deciding which is followed. Under conditions where the breakdown of the intermediate α-hydroxy-amine is rate-limiting, *i.e.* at relatively low pH, there is evidence[4] that hydrolysis of imines of the type Ph$_2$C=NR (R = H or cyanoalkyl) is specific acid–general base-catalysed. Under conditions of relatively high pH, however, our results are consistent with rate-limiting nucleophilic addition to the ferrocenyliminium ion, as indicated earlier.

## Experimental

Methods of synthesis of the PF$_6^-$ salts of the iminium ions (1) and (3), and the identification of products of hydrolysis (2)

---

* The intermediacy of zwitterions akin to (8) has been postulated in amine addition to carbonyl compounds and in hydrolysis of the corresponding imines.[4]

and deprotonation (4) have been reported.[9] Acetonitrile was purified as described previously.[7a]

*Rate Measurements.*—For general remarks concerning rate measurements, see ref. 7. Reactions were followed spectrophotometrically at 25.0 °C by monitoring the loss of absorbance of the iminium ion either in the u.v. region (260—320 nm) where $\log \varepsilon = ca.\ 4$ or in the visible region (480—550 nm) where $\log \varepsilon = ca.\ 3.3$. The following wavelengths (nm) were used for reactions of the individual ions in water (values in parentheses are for reactions in $H_2O$–MeCN): (1a), 290, 500 (500); (1b), 295, 500 (500); (1c), 500 (500); (1d), 300 (298); (1e), 300 (300); (1f), 310 (290); (3a), 290; (3b), 285; (3c), 290, 500; (3d), 550; (3e), 550; (3f), 550. Reactions were followed through at least three half-lives and at least two separate determinations of each rate constant were carried out. Rate constants determined using different wavelengths were in good agreement. The concentration of iminium ion was generally $\leqslant 10^{-4}$M. Reactions with $HO^-$ were generally carried out with $10^{-3}$–$10^{-2}$M-NaOH. For reactions of the iminium ions (3), carbonate buffer ($10^{-2}$M) was used. The $[HO^-]$ was calculated from the pH, which was measured directly in each reaction solution.

All reactions were first-order and the rate constants ($k_\psi$) were calculated using a least-squares best-fit computer program; correlation coefficients were at least 0.999. The rate and equilibrium constants $k^{HO}$, $k^{H_2O}$, and $K_a$ were calculated as indicated in the Results section and are in Tables 1—4.

## Acknowledgements

We thank Dr. Norman Cully (New University of Ulster) for the preparation of iminium salts. Support of this work by the National Science Foundation (Chemical Dynamics) and the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. The collaboration of M. H. J. was made possible by the U.S.–India Exchange of Scientists Programme.

## References

1 See ' Iminium Salts in Organic Chemistry,' eds. H. Böhme and H. G. Viehe, *Adv. Org. Chem.*, 1976, vol. 9, part 1; 1979, vol. 9, Part 2; G. Tennant in ' Comprehensive Organic Chemistry,' ed. I.O. Sutherland, Pergamon, New York, 1979, vol. 2, ch. 8.
2 A. V. Willi, *Helv. Chim. Acta*, 1956, **39**, 1193; E. H. Cordes and W. P. Jencks, *J. Am. Chem. Soc.*, 1962, **84**, 832; R. L. Reeves and W. F. Smith, *ibid.*, 1963, **85**, 724; and refs. cited therein.
3 (*a*) E. H. Cordes and W. P. Jencks, *J. Am. Chem. Soc.*, 1963, **85**, 2843; (*b*) K. Koehler, W. Sandstrom, and E. H. Cordes, *ibid.*, 1964, **86**, 2413.
4 J. M. Sayer and P. Conlon, *J. Am. Chem. Soc.*, 1980, **102**, 2013.
5 H. Böhme and G. Auterhoff, *Chem. Ber.*, 1971, **104**, 2013.
6 W. E. Watts, *J. Organomet. Chem. Library*, 1979, **7**, 399.
7 (*a*) C. A. Bunton, N. Carrasco, and W. E. Watts, *J. Chem. Soc., Perkin Trans. 2*, 1979, 1267; (*b*) C. A. Bunton, N. Carrasco, F. Davoudzadeh, and W.E. Watts, *ibid.*, 1980, 1520; (*c*) 1981, 924; (*d*) C. A. Bunton, N. Carrasco, N. Cully, and W. E. Watts, *ibid.*, 1980, 1859; (*e*) C. A. Bunton, F. Davoudzadeh, and W. E. Watts, *J. Am. Chem. Soc.*, 1981, **103**, 3855.
8 P. Dixneuf and R. Dabard, *J. Organomet. Chem.*, 1972, **37**, 167; D. Mourot and H. Patin, *ibid.*, 1976, **114**, 89.
9 N. Cully and W. E. Watts, *Synth. React. Inorg. Metal-Org. Chem.*, (*a*) 1980, **10**, 289; (*b*) 1981, **11**, 695.
10 C. J. Cardin, S. Costa, T. J. King, N. Cully, and W. E. Watts, in preparation.
11 A. M. Easton, M. J. A. Habib, J. Park, and W. E. Watts, *J. Chem. Soc., Perkin Trans. 2*, 1972, 2290.
12 C. D. Ritchie, *Acc. Chem. Res.*, 1972, **5**, 348; *J. Am. Chem. Soc.*, 1975, **97**, 1170; *Pure Appl. Chem.*, 1978, **50**, 1281; C. D. Ritchie and P. O. I. Virtanen, *J. Am. Chem. Soc.*, 1972, **94**, 4966.
13 C. J. Cardin, W. Crawford, W. E. Watts, and B. J. Hathaway, *J. Chem. Soc., Dalton Trans.*, 1979, 970.
14 (*a*) C. A. Bunton and S. K. Huang, *J. Am. Chem. Soc.*, 1972, **94**, 3536; (*b*) M. J. Postle and P. A. H. Wyatt, *J. Chem. Soc., Perkin Trans. 2*, 1972, 474.
15 See R. P. Bell, *Adv. Phys. Org. Chem.*, 1966, **4**, 1.
16 C. A. Bunton and S. K. Huang, *J. Am. Chem. Soc.*, 1974, **96**, 515; C. D. Ritchie, D. J. Wright, D.-S. Huang, and A. A. Kamego, *ibid.*, 1975, **97**, 1163; P. H. Ride, P. A. H. Wyatt, and Z. M. Zochowski, *J. Chem. Soc., Perkin Trans. 2*, 1974, 1188.
17 C. G. Swain and C. B. Scott, *J. Am. Chem. Soc.*, 1953, **75**, 141.

*Received* 18*th June* 1983; *Paper* 3/1012