Nucleophilic Addition to Ferrocenyl-stabilised Carbocations: the Nature of the Transition State

By **Clifford A. Bunton,** **Nelson Carrasco,** and **Faegh Davoudzadeh,** 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 for reactions of p-MeOC$_6$H$_4\overset{+}{C}$HFc (1a) (Fc = ferrocenyl), Fc$_2\overset{+}{C}$H (1b), Fc$_2\overset{+}{C}$Ph (1c), and FcĊHCH= CHFc (1d) with nucleophiles in water and water–acetonitrile can be approximately correlated with the N_+ scale. There is a good correlation with rate constants for nucleophilic addition to (p-MeOC$_6$H$_4$)$_3$C$^+$ in water, except for bulky amines. Reactivities of bulky amines towards a secondary carbocation are always greater than predicted by comparison with reactivities towards a tertiary carbocation, suggesting steric hindrance to the latter reaction. These steric effects are much smaller if comparisons of reactivity are between two secondary carbocations, e.g. (1a and b). The secondary α-hydrogen kinetic isotope effects (k^H/k^D) for reactions of (1a and b) are ca. 1.0 with anionic nucleophiles, ca. 0.96 with primary amines, and ca. 0.9 with water, and depend on the nature of the nucleophile and not its reactivity.

NUCLEOPHILIC additions to preformed triarylmethyl and tropylium cations have been studied extensively, especially with regard to relations between rate and equilibrium constants for addition.[1-5] Ritchie has shown [1] that the reactivities of nucleophiles towards these cations follow the N_+ scale; values of N_+ are estimated from expression (1) where k is the second-order rate con-

$$\log k = \log k_0 + N_+ \qquad (1)$$

stant for nucleophilic addition and k_0 is the rate constant for addition of a reference nucleophile (e.g. water) to a given cation. For a wide range of nucleophiles, N_+ is characteristic of the nucleophile but independent of the cation, whereas k_0 is characteristic of the cation. This scale was originally developed [1a] for additions to carbocations and diazonium ions, and deviations from equation (1) are usually <0.5 log unit although very large rate differences are covered. However, somewhat paradoxically, relatively large discrepancies are found for addition of water, and an averaging procedure has been used to assign N_+ values. Ritchie suggests that these deviations arise because water addition can be general base catalysed; tertiary amines catalyse addition of water to triarylmethyl cations.[1,3,4] The N_+ scale has also been successfully applied to the addition step of nucleophilic attack on non-ionic electrophiles, e.g. in nucleophilic aromatic substitutions and in some de-acylations.[1c]

The success of the N_+ correlation suggests that the reactivity–selectivity principle is not generally applicable to nucleophilic addition,† but this view has not been universally accepted. For example, Scott et al. have pointed out [5a] that a line of slope 0.8 can be drawn
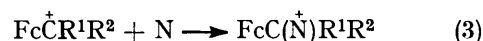
† Rappoport has compared [6] the apparent success of the reactivity–selectivity principle in the trapping of carbocations generated in S_N1 reactions with its failure in nucleophilic additions to preformed carbocations. Trapping of a reactive carbocationic intermediate by a reactive nucleophile should be diffusion-controlled, whereas reactions with unreactive nucleophiles will be activated. This difference leads to selectivity in the nucleophilic trapping of a series of kinetically generated carbocations.

through the points of a plot of $\log k$ against N_+ for addition of a variety of nucleophiles to An$_3$C$^+$ (An = p-MeOC$_6$H$_4$) and that this line includes the datum point for water addition, whereas this point is off a line of unit slope. It was therefore suggested that equation (1) should be modified to include a selectivity parameter (S_+) characteristic of the cation, i.e. equation (2) with

$$\log k = \log k_0 + S_+ N_+ \qquad (2)$$

$S_+ = 0.8$ for An$_3$C$^+$. However, only a limited amount of data was treated in this study and the general validity of the N_+ scale in its original form is very impressive.[1b,c]

Attempts have been made to rationalise the success of the N_+ correlation in terms of both ' early ' and ' late ' transition states [1,7] but, with most electrophiles studied to date, there is no simple way of estimating the extent of change of hybridisation of the atom at the reaction centre of the electrophile. Furthermore, it is difficult to study the effect of the steric characteristics of the electrophile using the conventional system (viz. nucleophilic additions to triarylmethyl cations) although such studies are possible with non-ionic electrophiles.[1c] These limitations are removed by studying additions of nucleophiles (N) to ferrocenylalkylium ions [equation (3)] where primary, secondary, and tertiary carbocations can be used.[8,9] The groups R^1,R^2 can by hydrogen, alkyl,

$$\text{Fc}\overset{+}{\text{C}}\text{R}^1\text{R}^2 + \text{N} \longrightarrow \text{FcC}(\overset{+}{\text{N}})\text{R}^1\text{R}^2 \qquad (3)$$

aryl, or metallocenyl; their bulk can be varied widely and alkyl groups may include a β-hydrogen atom so that concomitant nucleophilic addition and deprotonation can be studied.[9c] In addition, one can measure the α-hydrogen isotope effect on rates of additions to secondary systems and thereby evaluate the change in orbital hybridisation at the reaction site in formation of the transition state.[9b]

Extensive studies have been made of the rates of S_N1 reactions of ferrocenylalkyl substrates [10] and of the equilibria between 1-ferrocenylalkanols and related

carbocations in aqueous acid,[8,11] which show that the ferrocenyl group is very effective in stabilising a carbo-cationic centre. Various structural models have been considered.[10b] The stereochemistry of nucleophilic

a; $R^1 = H$, $R^2 = An$
b; $R^1 = H$, $R^2 = Fc$
c; $R^1 = Ph$, $R^2 = Fc$
d; $R^1 = H$, $R^2 = trans-CH=CHFc$
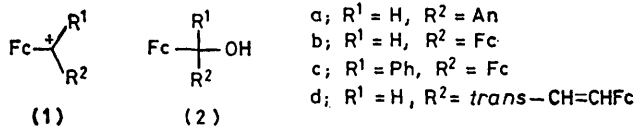
(Fc = ferrocenyl; An = p-methoxyphenyl)

addition and deprotonation reactions of ferrocenyl-alkylium ions, and of the reverse reactions, has also been investigated and it has been shown that these reactions proceed preferentially from the *exo*-face of the penta-fulvene-like ligand of the carbocations.[9d,10]

In the present work,[9a, b] we have measured the rates of addition of a variety of neutral and anionic nucleophiles in water and water–acetonitrile (1 : 1 w/w) to the secondary carbocations (1a and b), the tertiary carbocation (1c), and the allylic carbocation (1d). Methods of preparation of the tetrafluoroborates of these cations and of the alcohol precursors (2a—d) are in the Experimental section.

RESULTS

Reactions in Water.—Additions of a variety of neutral and anionic nucleophiles to the secondary carbocation (1a) in water at 25 °C were studied. Second-order rate constants, which cover a *ca.* 2 × 10^5-fold change, are in Table 1 which
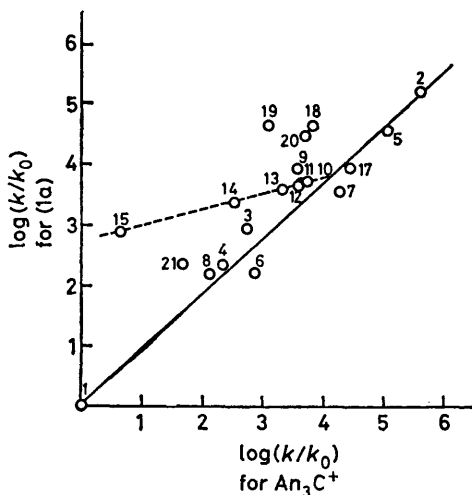

FIGURE 1 Relation between $\log(k/k_0)$ values for nucleophilic additions to p-MeOC$_6$H$_4$ĊHFc (1a) and An$_3$C$^+$ in water at 25.0 °C; nucleophiles numbered as in Table 1

also includes N_+ and (N_+) values (see later), a few rate constants for additions to the other secondary carbocation (1b), and $\log(k/k_0)$ values [3] for additions to An$_3$C$^+$. Because of the low solubility in water of products of addition to (1b), it was necessary to use a low initial concentration of sub-strate to avoid precipitation; the rate constants for hydride addition (nucleophiles 5—7; Table 1) giving diferrocenyl-methane, the least soluble of the products, are the least reliable for this reason.

The similarity in reactivity towards nucleophiles of the cations (1a) and An$_3$C$^+$ is shown by a plot (Figure 1) of $\log(k/k_0)$ values for reactions in water. Most of the points lie within 0.5 log unit of a line of unit slope drawn through the origin. This correlation is not too surprising because these cations have similar reactivities towards water.[3a,8] However, the $\log(k/k_0)$ values for the secondary amines (nucleophiles 18—21) and some of the primary amines (particularly nucleophiles 14 and 15) differ markedly; the bulkier the amine, the slower is addition to An$_3$C$^+$ relative to (1a). Thus, a reasonably good straight line of slope 0.25 (broken line; Figure 1) can be drawn through the points for reactions with the series of increasingly bulky primary amines, *viz.* MeNH$_2$, EtNH$_2$, Pr^{i}NH$_2$, and Bu^{t}NH$_2$, and all the secondary amines react faster with (1a) than predicted from their reactivities towards An$_3$C$^+$ or Malachite Green (MG)$^+$, as indicated by the N_+ scale (Table 1). A

TABLE 1

Rate constants for reactions in water [a]

Nucleophile [b]	N_+ or (N_+) [c]	FcĊHAn (1a) k [d]	Fc$_2$ĊH (1b) k [d]	An$_3$C$^+$ log (k/k_0) [e]
1 H$_2$O	0	43.2	0.03 [f]	0
2 N$_3^-$	7.6	7.4 × 10^6	2.5 × 10^3	5.62
3 HO$^-$	4.75	3.66 × 10^4	21.9	2.74
4 CN$^-$	3.67	9.1 × 10^3		2.35
5 BH$_4^-$	(5.18) [g]	1.5 × 10^6	95.3	5.03
6 BH$_3$CN$^-$	(4.11) [g]	7.4 × 10^3	28	2.88
7 BDHNA [h]	(5.11) [g]	1.45 × 10^5		4.24
8 NH$_3$	(4.1) [i]	6.5 × 10^3	4.43	2.12
9 PhCH$_2$NH$_2$	(5.6) [i]	3.4 × 10^5		3.59
10 MeNH$_2$	(5.7) [i]	2.3 × 10^5	1.22 × 10^2	3.72
11 Bu^{n}NH$_2$	(5.6) [i]	2.2 × 10^5		3.60
12 Pr^{n}NH$_2$	5.55	2.0 × 10^5		3.62
13 EtNH$_2$	5.31	1.7 × 10^5		3.32
14 Pr^{i}NH$_2$	(4.6) [i]	9.9 × 10^4	43	2.55
15 Bu^{t}NH$_2$	(2.6) [i]	3.5 × 10^4		0.62
16 MeONH$_2$	3.88	1.2 × 10^4		
17 N$_2$H$_4$	5.66	3.75 × 10^5	2.75 × 10^2	4.43
18 Me$_2$NH	(5.8) [i]	1.8 × 10^6		3.82
19 Morpholine	5.25	1.8 × 10^6		3.10
20 Piperidine	6.11	1.3 × 10^6		3.70
21 Imidazole	3.66	9.6 × 10^3	5.00	1.67

[a] At 25.0 °C. [b] Sodium salts of anions were used. [c] See text. [d] Values in 1 mol^{-1} s^{-1} except for H$_2$O where the value is the first-order rate constant in s^{-1}. [e] Values from refs. 3a and b. [f] Estimated by extrapolation of rate constants for HO$^-$ in H$_2$O. [g] Estimated from rate constants for (MG)$^+$.[3b,c] [h] 1-Benzyl-1,4-dihydronicotinamide. [i] From equation (5); see text.

possible interpretation, discussed later, is that steric hindrance to nucleophilic additions to propellor-shaped [12] triarylmethyl cations is much more important than for additions to a secondary carbocation such as (1a). If this is correct, it would be preferable in estimation of relative nucleophilicity parameters to use kinetic data for reactions of secondary carbocations rather than triarylmethyl cations upon whose rates N_+ values were originally based.[1a]

From the limited evidence from reactions of the difer-rocenylmethyl cation (1b) in water (Table 1), it is apparent that relative reactivities (k/k_0) are similar to those for (1a), with the latter cation being *ca.* 10^3 times more reactive towards each nucleophile for which comparison can be made.

Reactions in Aqueous Acetonitrile.—Because of problems of insolubility of products in water, nucleophilic additions to the diferrocenyl-substituted carbocations (1b—d) were generally studied in water–acetonitrile (1 : 1 w/w) at 25 °C. The second-order rate constants are in Table 2 which also

includes results for reactions of (1a) in the same solvent. Reactivity towards addition decreased through the series, (1a) > (1d) > (1b) > (1c). Rate constants for reactions of (1a and b) in the mixed solvent tend to be greater than those for reactions in water (Tables 1 and 2); this holds for additions of amines as well as anionic nucleophiles. The

A comparison of relative reactivities of a secondary and a tertiary ferrocenylalkylium ion is shown in Figure 3 in which $\log(k/k_0)$ values for (1b and c) are plotted. Most points lie close to a line of unit slope through the origin, but again the rate constants for addition of bulky amines (particularly $\mathrm{Bu^tNH_2}$) to the secondary carbocation (1b)

TABLE 2

Rate constants for reactions in water–acetonitrile (1 : 1 /w) [a,d]

	Nucleophile [b]	FcĊHAn (1a)	Fc$_2$ĊH (1b)	Fc$_2$ĊPh (1c)	Fc(ĊH)$_3$Fc (1d)
1	H_2O	58.0	2.66×10^{-2}	2.8×10^{-4}	2.5
2	N_3^-		2.61×10^4	8.3×10^2	ca. 5×10^6
3	HO^-	4.3×10^4	38.7	0.28	1.6×10^4
5	BH_4^-		1.89×10^3	46.	3.8×10^5
6	BH_3CN^-	6.4×10^4	62	2.16	1.3×10^4
7	BDHNA [h]		ca. 47 [e]	0.42	
10	$MeNH_2$		6.53×10^2	21.4	2.4×10^5
13	$EtNH_2$		4.03×10^2	8.4	
14	Pr^iNH_2		1.81×10^2	0.75	
15	Bu^tNH_2		34.7	4.6×10^{-3}	2.2×10^4
16	$MeONH_2$	5.0×10^5	21.8		
17	N_2H_4		3.80×10^2	8.57	
18	Me_2NH		3.43×10^3	60.8	
19	Morpholine		1.93×10^3	5.64	
20	Piperidine		3.10×10^3	53.0	
21	Imidazole	7.5×10^4	26	0.53	
22	Pr^i_2NH		3.15	8.3×10^{-3}	
23	DABCO			1.22×10^{-3}	
24	PhS^-			9.6×10^4	

[a,b,d,h] As for Table 1.   [e] Reaction was not strictly first order with respect to [BDHNA].

pattern of relative reactivities of the three secondary carbocations in the different solvents is similar, as shown by a plot (Figure 2) of $\log(k/k_0)$ for additions to (1a) in water and to (1b and d) in aqueous acetonitrile. Most points lie within one log unit of a line (unbroken) drawn with unit slope through the origin, but a better correlating line (broken) can be drawn also with unit slope but excluding the point for water addition (i.e. the origin). The deviations noted

are higher than predicted from the relative reactivities of the tertiary (1c). Thus, steric hindrance to addition of bulky nucleophiles to tertiary carbocations is not a feature peculiar to triarylmethyl cations, although the magnitude
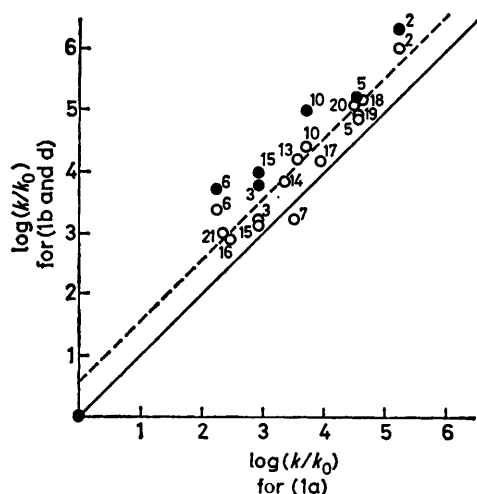

FIGURE 3 Relation between $\log(k/k_0)$ values for nucleophilic additions to Fc$_2$ĊH (1b) and Fc$_2$ĊPh (1c) in water–acetonitrile (1 : 1 w/w) at 25.0 °C; nucleophiles numbered as in Table 2

FIGURE 2 Relation between $\log(k/k_0)$ values for nucleophilic additions to Fc$_2$ĊH (1b) (O) and FcĊHCH=CHFc (1d) (●) in water–acetonitrile (1 : 1 w/w) and to p-MeOC$_6$H$_4$ĊHFc (1a) in water at 25.0 °C; nucleophiles numbered as in Table 1

earlier in comparison of reactivities of bulky amines towards secondary and tertiary carbocations (Figure 1) are absent in this comparison of relative reactivities of secondary ferrocenylalkylium ions.
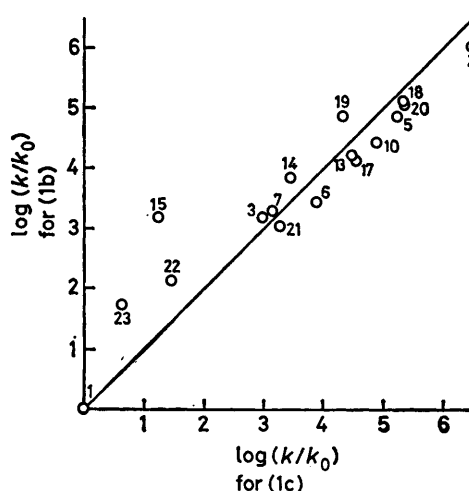
of the effect is larger for these systems than for (1c); cf. for additions of t-butylamine in the solvent indicated, $\log(k/k_0)$ values for An_3C^+, (1a), (1b), (1c), and (1d) are 0.62 (H_2O), 2.93 (H_2O), 3.16 (H_2O–MeCN), 1.20 (H_2O–MeCN), and 3.94 (H_2O–MeCN), respectively. Both the highly hindered di-isopropylamine and the tertiary amine DABCO (1,4-diazabicyclo[2.2.2]octane) are more reactive towards the secondary carbocation (1b) than would be expected from their reactivities towards the tertiary (1c). However, these amines are acting as general base catalysts of water addition,

giving alcohol and not amine as product (see Experimental section).

Comparison of the relative reactivities of the two tertiary carbocations An_3C^+ and (1c) is shown in Figure 4. The cor-
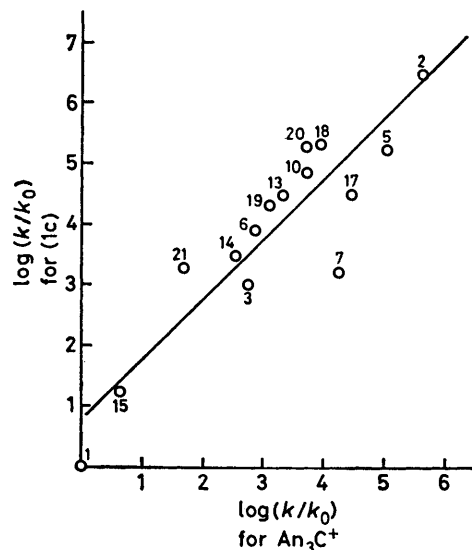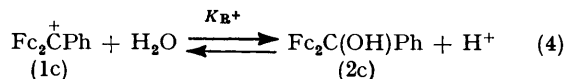

FIGURE 4 Relation between $\log(k/k_0)$ values for nucleophilic additions to $Fc_2\overset{+}{C}Ph$ (1c) in water–acetonitrile (1 : 1 w/w) and to An_3C^+ in water at 25.0 °C; nucleophiles numbered as in Table 1

respondence of $\log(k/k_0)$ values is remarkably close despite the differences in solvent and in structural type.

The second-order rate constants for acid heterolysis of the secondary alcohols (2a,b, and d) in water–acetonitrile (1 : 1 w/w) at 25 °C have already been reported;[8] the corresponding constant for the tertiary alcohol (2c) is 4.35 l mol^{-1} s^{-1}, giving a pK_{R^+} value of 4.19 in the mixed solvent [equation (4)]. The corresponding pK_{R^+} values for the

$$Fc_2\overset{+}{C}Ph + H_2O \underset{}{\overset{K_{R^+}}{\rightleftharpoons}} Fc_2C(OH)Ph + H^+ \qquad (4)$$
$$\text{(1c)} \qquad\qquad\qquad \text{(2c)}$$

cations (1a), (1b), (1d), and An_3C^+ in the same solvent are 0.46, 3.15, 4.18, and 0.08, respectively.[8]

Correlations with N_+ *Values.*—Values of N_+ (Table 1) have been assigned for fewer than half the nucleophiles used in this study. Those which have been given have been obtained [1b] by a statistical procedure which averages kinetic data for reactions of the nucleophiles with several cationic and neutral electrophiles (*e.g.* additions to triarylmethyl cations, deacylation reactions). For the other nucleophiles, values of (N_+) (given in parentheses in Table 1) have been calculated from $\log(k/k_0)$ values for additions to $(MG)^+$ and An_3C^+ in water at 25 °C.[3] These log values are not directly comparable with literature N_+ values obtained by the aforementioned averaging procedure. However, values based upon rates of reaction of An_3C^+ have been found [3] to be systematically *ca.* 2 log units lower than the averaged N_+ values where direct comparison can be made. In these cases, the (N_+) values have been calculated accordingly from equation (5). This arbitrary procedure gives values which are not unreasonable, as shown later.

$$(N_+) = \log(k/k_0)_{An_3C^+} + 2.0 \qquad (5)$$

A plot (Figure 5) of $\log(k/k_0)$ values for reactions of (1a) in

water against N_+ or (N_+) is approximately linear with slope of *ca.* 0.7, and the point for water (*i.e.* the origin) lies on this line. Alternatively, a line (broken) of unit slope can be drawn provided the point for water is excluded; most of the points lie within 0.5 log unit of this line except those for bulky amines, particularly t-butylamine, whose $\log(k/k_0)$ values for reactions of (1a) are much higher than predicted.

TABLE 3

Secondary α-hydrogen kinetic isotope effects on solvolysis[a]

Rate constants and k.i.e.[b]	$Fc\overset{+}{C}HAn$ (1a) in H_2O	$Fc_2\overset{+}{C}H$ (1b)	
		In H_2O–MeCN [c]	In H_2O–MeOH [c]
k_f^H/s^{-1}	43.2	2.66 × 10^{-2}	0.177
k_f^D/s^{-1}	49.4	2.91 × 10^{-2}	0.198
k_r^H/l mol^{-1} s^{-1}	1.05 × 10^3	37.2	
k_r^D/l mol^{-1} s^{-1}	9.13 × 10^2	34.4	
k_f^H/k_f^D	0.874 ± 0.016	0.915 ± 0.024	0.896 ± 0.010
k_r^H/k_r^D	1.15 ± 0.07	1.08 ± 0.02	
$K_{R^+}{}^H/K_{R^+}{}^D$	0.76	0.85	

[a] At 25.0 °C. [b] K.i.e. are given with their standard deviations. [c] Mole fraction of H_2O 0.695.

Secondary α-*Hydrogen Kinetic Isotope Effects.*—We have measured the effect upon reaction rates of replacement of the methine ($\overset{+}{C}H$) hydrogen of (1a and b) by deuterium. Methods of preparation of the alcohol precursors of these [2]H-labelled carbocations are in the Experimental section. For reactions with water, rate constants for both the forward (k_f) and reverse (k_r) reactions [equation (6)] were determined (Table 3). Because of solubility problems,

$$(1) + H_2O \underset{k_r}{\overset{k_f}{\rightleftharpoons}} (2) + H^+ \qquad (6)$$
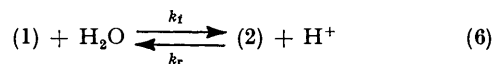
solvolyses of the diferrocenylmethyl substrate (1b) were followed only in aqueous acetonitrile and in aqueous methanol. Because reaction with the latter solvent gives a
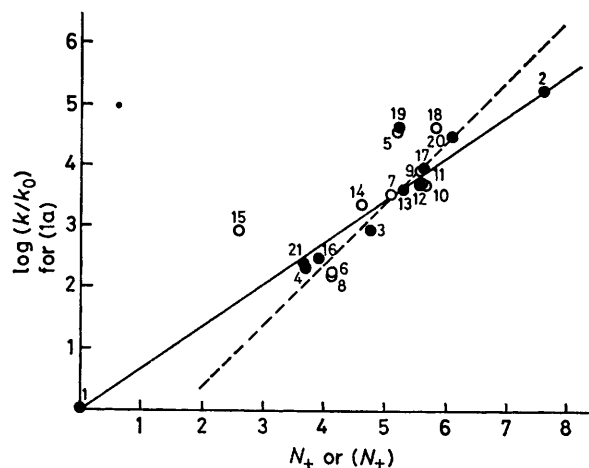

FIGURE 5 Plot of $\log(k/k_0)$ values for nucleophilic additions to p-MeOC$_6$H$_4\overset{+}{C}HFc$ (1a) in water at 25.0 °C against N_+ (●) or (N_+) (○) values; nucleophiles numbered as in Table 1

mixture of alcohol and methyl ether, the rate constant for acid heterolysis of the alcohol (2b) was determined only for reaction in aqueous acetonitrile. The isotope effects upon rates of addition of the other nucleophiles were determined (Table 4) only for reactions of the diferrocenylmethyl cation (1b) in aqueous acetonitrile.

There is no secondary α-hydrogen kinetic isotope effect

(k.i.e.) upon the rates of addition of anionic nucleophiles to (1b), within the accuracy (see Experimental) of our measurements (Table 4). However, there is a small isotope effect for additions of amines to (1b) and a larger effect (*ca.* 10%) for reactions of (1a and b) with water (Tables 3 and 4). These effects are not related to the reactivity of the nucleophile; thus, the same k.i.e. is associated with additions of a reactive (MeNH$_2$) and a relatively unreactive α-effect amine

TABLE 4

Secondary α-hydrogen kinetic isotope effects

on nucleophilic additions to $\overset{+}{Fc_2CH}$ (1b) [a]

Nucleophile [b]	$k_f{}^H$/l mol^{-1} s^{-1}	$k_f{}^H/k_f{}^D$ [c]
HO$^-$	38.7	0.987 $\pm$ 0.020
BH$_4{}^-$	1.89 $\times$ 10^3	0.999 $\pm$ 0.020
N$_3{}^-$	2.61 $\times$ 10^4	1.012 $\pm$ 0.013
MeNH$_2$	6.53 $\times$ 10^2	0.955 $\pm$ 0.010
Bu^{t}NH$_2$	34.7	0.969 $\pm$ 0.014
MeONH$_2$	21.8	0.957 $\pm$ 0.004
H$_2$O	2.66 $\times$ 10^{-2} [d]	0.915 $\pm$ 0.024

[a] In water–acetonitrile (1 : 1 w/w) at 25.0 °C. [b] As for Table 1. [c] Standard deviations are given. [d] In s^{-1}

(MeONH$_2$). The effect is slightly smaller for the very bulky t-butylamine but the difference is within experimental error.

The secondary α-hydrogen isotope effects upon carbocation $\rightleftharpoons$ alcohol equilibria in aqueous acidic media ($K_{R^+}{}^H/K_{R^+}{}^D$ values; Table 3) are as expected [13] for reactions involving $sp^2 \rightleftharpoons sp^3$ change in hybridisation at the reaction site and are about twice as large as the k.i.e. upon alcohol heterolysis, in accord with the $k_f{}^H/k_f{}^D$ values for water addition. The secondary α-hydrogen k.i.e. for acid heterolysis of diphenylmethanol has been estimated [14] indirectly to be 1.08, based upon measurements of the rates of permanganate oxidation of Ph$_2$CHOH and Ph$_2$C[^{2}H]OH. Our $k_r{}^H/k_r{}^D$ values are very similar, suggesting that the presence of the metal atom is not complicating our interpretation.*

Replacement of acetonitrile in aqueous acetonitrile by an equimolar amount of methanol, a more nucleophilic solvent (*cf.* N_+ values [1a]), sharply increases k_f but only slightly increases the inverse isotope effect $k_f{}^H/k_f{}^D$ (Table 3), suggesting that our qualitative conclusions concerning the spontaneous addition reaction (see later) are unaffected by changes in the medium although these may well affect the numerical value of k^H/k^D.

DISCUSSION

Kinetic Isotope Effects.—The absence of a secondary α-hydrogen k.i.e. upon additions of anionic nucleophiles to the diferrocenylmethyl cation (1b) (Table 4) shows that there is little or no change in orbital hybridisation from sp^2 at the reaction centre (C$_\alpha$) of the carbocation† on going to the transition states for addition, which are therefore satisfactorily described by an ion-pair model with encounter and desolvation of the nucleophile being the major free-energy barriers to reaction. This conclusion, which also applies to the reverse reactions, is consistent with the solvent effect on rates of nucleophilic additions to the carbocations (Tables 1 and 2) and with kinetic data for S_N1 reactions of triarylmethyl [1-4] and

* A secondary k.i.e. (k^H/k^D 1.06 $\pm$ 0.04) has been measured [15] for solvolyses of $\overset{+}{FcCX_2NMe_3}$ I$^-$ (X = H and ^{2}H) in water.

ferrocenylalkyl [10] substrates. However, the secondary k.i.e. for addition of water to the carbocations (1a and b) (Table 3) suggests that here there is appreciable orbital rehybridisation at C$_\alpha$ from sp^2 towards sp^3 in formation of the transition state; this conclusion also applies for additions of amines (Table 4) although the change is much smaller. It follows that C $\cdots$ N bond-making has made some progress in the transition state for amine addition but much less than the extent of C $\cdots$ O bond-making in the transition state for water addition.

These isotope effects are not in accord with models which postulate ' late ' transition states (*cf.* ref. 7) but are completely consistent with Ritchie's suggestion [1] that deviations of water from the N_+ scale arise because its addition to carbocations is governed by different factors from those which control additions of anions. They also suggest that hydroxide ion is behaving like other anionic nucleophiles and there is no reason to believe that it is acting as a general base by activating addition of a water molecule. (A general base catalysed addition of water in which the proton is transferred completely to the catalysing base is indistinguishable from direct addition of hydroxide.)
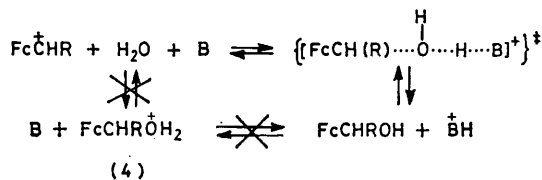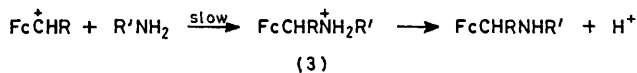
Additions of both water and primary amines to carbocations involve proton loss, and the observations [1,3,4] of general base catalysis of water addition show that C $\cdots$ O bond-making is concerted with proton loss from oxygen. General base catalysis is relatively unimportant in additions of amines to carbocations [3] but, for these reactions, encounter and probably loss of a water molecule hydrogen-bonded to the amino-group contribute to the free-energy barrier to reaction; *cf.* the kinetic solvent effects (Tables 1 and 2). Our conclusion that there is some bond-making in the transition state for addition of amines but not for addition of anions is, however, consistent with Bruice's observation [17] that, for additions to (MG)$^+$, the free energies of activation and overall reaction could be correlated for reactions with amines but not with anionic nucleophiles.

Kinetic solvent hydrogen isotope effects (k.s.i.e.) have been measured for acid heterolysis of various alcohols including An$_3$COH [2] and several 1-ferrocenylalkanols.[8] The values ($k_r{}^{H_2O}/k_r{}^{D_2O}$ *ca.* 0.4) are in the range considered typical [13] of A-1 reactions which involve a pre-equilibrium proton transfer followed by rate-limiting C–O bond-breaking. However, this two-step mechanism is inconsistent with the observation of general base catalysis of water addition to preformed carbocations, and analysis of reaction rates shows [1] that acid heterolysis of An$_3$COH is almost certainly a concerted reaction, despite the observed k.s.i.e. Therefore, the k.s.i.e. does not distinguish between pre-equilibrium proton transfer and a concerted reaction when the proton is being transferred between electronegative atoms and there are appreciable inverse secondary and transfer isotope effects; a model has been proposed for conservation of

† The magnitudes (*ca.* 165 Hz) of the ^{13}Cα–H coupling constants in the ^{13}C n.m.r. spectra of secondary ferrocenylalkylium ions are consistent with sp^2 (but not sp^3) hybridisation at C$_\alpha$.[16]

zero-point energy associated with hydrogen in the concerted reaction (cf. ref. 18).

Transition States for Additions of Water and Amines.— The mechanistic difference (Scheme) between nucleophilic additions of water and amines, discussed earlier, can be rationalised in terms of the three-dimensional free-energy diagrams which are often used to discuss

$$Fc\overset{+}{C}HR + R'NH_2 \xrightarrow{slow} Fc CHR\overset{+}{N}H_2R' \longrightarrow Fc CHRNHR' + H^+$$

(3)

$$Fc\overset{+}{C}HR + H_2O + B \rightleftharpoons \{[Fc CH(R)\cdots\overset{H}{\overset{|}{O}}\cdots H\cdots B]^+\}^{\ddagger}$$

$$B + Fc CHR\overset{+}{O}H_2 \rightleftharpoons Fc CHROH + \overset{+}{B}H$$

(4)

SCHEME

reactions which may proceed by concerted or stepwise mechanisms.[19]

The possible pathways for a water-catalysed reaction of a carbocation R^+ with a non-ionic nucleophile XH are shown in Figure 6, where XH is water or a primary or secondary amine and water is the proton acceptor. (Contour lines are not included in Figure 6 in the interests of clarity and because they will differ for the reactions with water and with amines.) In principle, two stepwise pathways are possible, viz. (i) steps 1'—1", with $R\overset{+}{X}H$ as an intermediate, and (ii) steps 2'—2", involving initial deprotonation of XH followed by reaction of X⁻
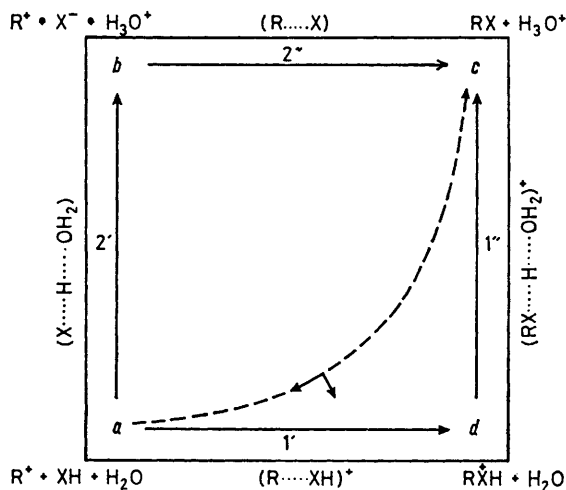

FIGURE 6 Free-energy diagram for addition of amines or water to a carbocation; the broken line gives a qualitative indication of the reaction co-ordinate for water addition.

with R^+. Pathway 2'—2" is highly improbable for reactions of either water or amine (cf. for the water reaction, this pathway is equivalent to reaction of R^+ with HO⁻, which will be unimportant in neutral or acidic solutions). Pathway 1'—1" is much more favourable when XH is an amine than when it is water because an oxonium ion [e.g. (4)] has a much higher

energy (relative to reactants) than the corresponding ammonium ion [e.g. (3)].

As has been pointed out,[19] concerted reactions avoid formation of highly energetic intermediates and the associated high-energy transition states. Thus, while amine addition to R^+ could follow pathway 1'—1" via the relatively stable protonated amine (point d), or a pathway close to 1'—1", the reaction co-ordinate for water addition will follow the broken line (Figure 6) avoiding the intermediacy of an oxonium ion, i.e. one could alternatively describe water addition to R^+ as an S_E2 reaction on water.[20] The Brønsted parameter β is related to the position of the transition state in the direction $a \longrightarrow b$ and its value appears to be relatively small for the general base catalysed addition of water to triarylmethyl cations.[3,4] For example, a relatively strong base (e.g. a tertiary amine) is required in order to observe general catalysis, and a weak base such as a carboxylate ion is ineffective relative to the total proton-accepting power of the bulk solvent water.[2-4] In exactly the same way, a carboxylic acid is usually too weak to catalyse alcohol heterolysis. However, the position of the transition state on the pathway from a to d will be related to the free energy of the carbocation and, as it is made more reactive, its free energy (position a) will increase relative to that of protonated alcohol (position d). The reaction co-ordinate will then move towards pathway 1'—1" (i.e. $a \longrightarrow d \longrightarrow c$), as indicated by the resultant of the arrows in Figure 6, and in the limit the reaction will become stepwise. The value of α will tend to unity and heterolysis of the alcohol will become specific hydrogen-ion catalysed. Such behaviour is that expected for heterolytic reactions, e.g. rearrangements of aliphatic alcohols. A similar pattern is followed in the hydrolysis of orthoesters and acetals where general acid catalysis is observed when the carbocationic intermediate is stabilised by electron-donating substituents.[21]

This interpretation of the changing nature of the transition state for the water reaction is consistent with Ritchie's observation[1] that the reactivity of water towards various electrophiles does not fit the predictions of the N_+ scale; indeed, it suggests that it should not. Therefore, there seems to be no reason for the introduction of an additional parameter [cf. equation (2)[5a]] simply to make a datum point for water conform to the N_+ scale.

Consideration of Figure 6 suggests that there should be appreciable orbital rehybridisation at C_α in the relatively ' late ' transition states for water addition to the cations (1a and b) as indicated by the secondary α-hydrogen k.i.e. (Table 3). However, addition of reactive nucleophiles is energetically ' downhill ' (i.e. $a \longrightarrow d$), and the Hammond postulate then predicts an ' early ' carbocation-like transition state for such reactions.

Our conclusions about the differences in the transition states for additions of water and of amines are qualitatively consistent with earlier observations[3,4] on the

kinetic salt effects for reactions of An_3C^+. Addition of water is inhibited by added inert salts, especially those with bulky anions which can ion-pair with the carbocation, and ferrocenylalkyl cations behave similarly.[8] There are similar negative salt effects on additions of anions (e.g. HO^- or N_3^-), but salt effects on amine additions are small.[3] Insofar as addition of water involves partial deprotonation in the transition state, a kinetically unimportant step in amine additions, one might expect to see parallel patterns of behaviour for additions of water and anions, as for example in the similarity of salt effects.

The original assignment [1a] of N_+ values was based upon a comparison of the reactivities of nucleophiles, including water, towards the relatively unreactive carbocations $(MG)^+$ and Crystal Violet. However, water is more reactive towards both An_3C^+ and (1a) than predicated by N_+, as discussed earlier. These differences are understandable in that a water molecule attacking the more reactive cations needs less assistance from another water molecule acting as a general base. If one regards these additions as S_E2 reactions on a water oxygen atom, it appears that the reactivity–selectivity principle applies to these substitutions but not to the electrophilic additions to the more reactive nucleophiles, e.g. anions and amines.

Structural Effects on Nucleophilic Addition.—The α-hydrogen k.i.e. for solvolysis is similar for the carbocations (1a) and (1b), despite a reactivity difference of more than 10^3 (Table 3). Thus, our general conclusions regarding the nature of the transition state for water addition * are probably applicable to most of the preformed carbocations whose reactions have been studied, although the relative extents of $C \cdots O$ bond-making and $O \cdots H$ bond-breaking almost certainly will vary (cf. ref. 1). For additions of other nucleophiles, there is apparently little bond-making in the transition states and no reactivity–selectivity relationship as evidenced by the success of the N_+ scale. Steric effects are important, however. Thus, even though additions of amines, for example, involve little orbital rehybridisation at C_α, the reactants must be sufficiently close in the transition state to hinder additions of bulky amines to tertiary carbocations such as An_3C^+ and (1c) (Figures 1—5). Therefore, steric effects can complicate the use of equation (1), especially in view of the fact that the original N_+ scale was based largely on reactions of triarylmethyl cations.[1a]

Both N_+ and $\log k_0$ values are solvent dependent,[1] but nonetheless we see correlation of values of $\log (k/k_0)$ for reactions of (1a) in water with those of (1b and d) in aqueous acetonitrile (Figure 2). Deviations from a line of unit slope are not large, even for reactions of the ambient electrophile (1d). However, the hydrophobicity of the nucleophiles may be playing a role because generally the bulky non-ionic nucleophiles are

less reactive in aqueous acetonitrile than predicted by the linear correlation in Figure 2. Such hydrophobic non-ionic nucleophiles should have their activity coefficients reduced the most by addition of an organic solvent to water. However, the effects are not large and one of these reactants, *viz.* 1-benzyldihydronicotinamide, may well be transferring hydrogen by two steps perhaps, each involving a single-electron transfer,[22] so that its rates of reaction may not be properly comparable with those of other nucleophiles which react by two-electron transfers.†

Steric Bulk of the Electrophile.—The evident importance of the bulk of the nucleophile in additions to the tertiary carbocations (1c) and An_3C^+, as compared with its apparent unimportance in additions to the secondary carbocations (1a, b, and d), represents a significant deviation from the simplicity of equation (1). Although triarylmethyl cations are conformationally mobile, there are considerable constraints upon coplanarity and at least one of the aryl rings must be twisted out of plane at any instant,[12] creating steric hindrance to addition of a bulky nucleophile. In the cation (1a), however, coplanarity of the aryl and cyclopentadienyl rings attached to C_α can be achieved with minimal steric repulsion, allowing relatively unhindered *exo*-addition of nucleophiles. Steric hindrance to additions to (1a) may be further diminished in importance by downward displacement of C_α towards the iron atom as has been indicated by molecular orbital calculations [24] and found in the crystal structures [25] of ferrocenyl-stabilised carbocation salts.

(5A)   (5B)
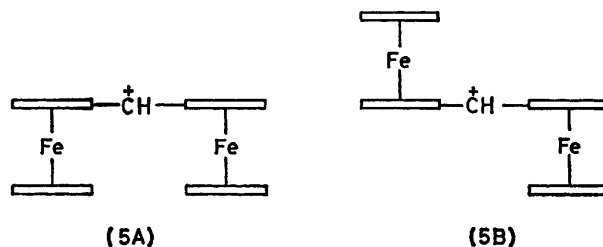
The situation is more complex for additions to the diferrocenylmethyl cation (1b) which can assume two conformations (5A and B) in which the cyclopentadienyl rings attached to C_α are coplanar and, presumably, resonance stabilisation is maximised. The *exo*-face of (5A) is open to unhindered nucleophilic attack whereas additions to the more favoured *anti*-conformer (5B) would be hindered by one or other of the $Fe(C_5H_5)$ residues. The apparent unimportance of steric effects in nucleophilic additions to (1b) suggests either that it reacts preferentially in the unfavoured *syn*-conformation (5A) or, more probably, in a *syn*-conformation in which repulsions are minimised by out of plane twisting of the $(C_5H_4)\overset{+}{C}H(C_5H_4)$ ligand and bending of the $(C_5H_4)–C^+$ bonds (cf. crystal structure [25a]) such that steric inter-

---

* The heterolysis of (2c) is catalysed by dichloroacetic acid (unpublished results) and such catalysis by a general acid is consistent with our conclusions regarding water addition to the carbocations.

† In aprotic solvents, ferrocenyl-stabilised carbocations react with tertiary amines by single-electron transfer, but primary and secondary amines add as nucleophiles.[23]

actions in the transition states for additions are minimised. Variable-temperature ^{1}H n.m.r. spectroscopic studies [25a] have shown that such twisting deformations can occur readily for (1b) in solution. In this connection, it may be noted that $\log(k/k_0)$ values for reactions in aqueous acetonitrile of (1b) are all lower by 0.5 ± 0.3 log unit than those for the vinologous allylic cation (1d) but that the difference is only slightly larger for reactions with the bulky t-butylamine than with methylamine (0.83 and 0.60 log unit, respectively; see Table 2). Because additions to (1d) should be relatively unhindered, steric hindrance to additions of bulky nucleophiles to (1b) therefore appears unimportant. In comparison with (1b), conformational mobility of the tertiary carbocation (1c) would be more restricted, and the presence of the phenyl group introduces additional steric encumbrance at the reaction site, so it is not unexpected that additions of bulky amines to (1c) are apparently hindered.

In summary, these observations suggest that N_+ values estimated from reactivities of triarylmethyl cations will not accurately reflect nucleophilicities of bulky amines (*e.g.* t-butylamine and secondary amines) towards less hindered electrophiles. However, apart from steric interactions, there is essentially no relation between reactivity and selectivity for nucleophilic additions to carbocations, except perhaps for water addition.

EXPERIMENTAL

For general remarks concerning experimental procedures, see ref. 26. Acetonitrile was purified as described previously.[8] Reagent-grade amines were purified by distillation or recrystallisation, as appropriate, immediately before use.

Preparation of Alcohols.—Methods of preparation of the alcohols (2a),[8] (2b),[27] (2c),[27] and (2d)[8] have been described. The deuteriated analogues of (2a and b) were obtained by reduction of p-methoxybenzoylferrocene[28] and diferrocenyl ketone,[27] respectively, with lithium aluminium deuteride in ether–benzene using procedures previously described.[26] Their m.p.s were almost identical with those of their all-protio analogues (2a and b);[8] their ^{1}H n.m.r. spectra (CDCl$_3$) were identical with those of the unlabelled compounds except for the absence of the methine proton resonance.

Preparation of Tetrafluoroborates of Cations (1).—These salts were prepared from the corresponding alcohols (2) by the method described[8] previously and were stored at low temperatures in the absence of light and moisture.

Rate Measurements.—Details of the methods of spectrophotometric determination of reaction rates have been described.[3,8] The slower reactions (half-life > 1 s) were followed using a Gilford spectrophotometer after addition of a freshly prepared solution (*ca.* 2 μl) of cation tetrafluoroborate in MeCN, CH$_2$Cl$_2$, or (CH$_2$Cl)$_2$ to the reaction solvent (*ca.* 3 ml) containing the nucleophile and following the decay with time of a suitable cation absorbance maximum [360 nm (1a); 348 nm (1b); 378 nm (1c); 417 nm (1d)]. The rates of the faster reactions were followed using a Durrum–Gibson stopped-flow spectrophotometer by mixing equal volumes of a solution of the cation in dilute acid (usually HCl) and a solution of the nucleophile in the same solvent

containing sufficient NaOH to neutralise the acid exactly. The rate constants determined in this way are inevitably less accurate than those obtained alternatively, particularly for reactive cations such as (1a) where much more concentrated acid is required to generate a workable initial concentration of carbocation [pK_{R+} values for (1a and b) in aqueous acetonitrile are 0.46 and 3.15, respectively[8]].

Solvolytic reactions were studied by an equilibrium displacement method. An equilibrium mixture of cation (1) and alcohol (2) in H$_2$O or H$_2$O–MeCN (1 : 1 w/w) containing acid (HCl or H$_2$SO$_4$) was mixed with an equal volume of acid-free solvent in the stopped-flow spectrophotometer. The rate at which the new equilibrium was established was determined by following the change in absorbance of carbocation and the rate constants were calculated from relationships (7)—(9) where k_ψ, k_f, and k_r are, respectively,

$$k_\psi = k_f + k_r[H^+] \qquad (7)$$

$$K_{R+} = k_f/k_r = [ROH][H^+]/[R^+]_{eq.} \qquad (8)$$

$$k_f = k_\psi/(1 + [H^+]/K_{R+}) = k_\psi/\{1 + ([R^+]/[ROH])_{eq.}\} \qquad (9)$$

the observed first-order rate constant, the first-order rate constant for addition of water, and the second-order rate constant for acid heterolysis of the alcohol.

All reactions were first order and rate constants (k_ψ) were evaluated using a least-squares best-fit computer program; correlation coefficients were at least 0.999. For most kinetic runs, *ca.* 15 data points were used and reactions were followed through at least four half-lives; results were reproducible. For measurement of the kinetic isotope effects, 8—12 individual runs were carried out for each nucleophile whose concentration was varied over a tenfold change; rate constants were evaluated using 30—50 data points. To avoid systematic errors, experiments were carried out with ^{2}H-labelled and unlabelled substrates alternately.

General Base Catalysed Hydrolyses.—Reaction of the cation (1c) with di-isopropylamine in aqueous acetonitrile gives the alcohol (2c) and not Fc$_2$C(NPr$^i{}_2$)Ph. This was shown as follows. After reaction was complete, the solution was carefully acidified by addition of 0.01M-HCl. If the amine product had been formed, the cation (1c) would have been generated at pH *ca.* 9, and would then have reacted slowly with water.[3b] However, the cation (1c) was formed only when the pH of the solution had been reduced to *ca.* 4, showing that it had been generated by acid heterolysis of the alcohol (2c),[8] rather than the amine. Similar results were obtained for reaction with DABCO in aqueous acetonitrile but, for reaction in the presence of dimethylamine, addition of acid to the resulting solution gave the cation (1c) at pH *ca.* 9, showing that the reaction product was Fc$_2$C(NMe$_2$)Ph.

REFERENCES

[1] (a) C. D. Ritchie, *Accounts Chem. Res.*, 1972, **5**, 348; (b) *J. Amer. Chem. Soc.*, 1975, **97**, 1170; C. D. Ritchie, D. J. Wright, D.-S. Huang, and A. A. Kamego, *ibid.*, p. 1163; C. D. Ritchie,

R. J. Minasz, A. A. Kamego, and M. Sawada, *ibid.*, 1977, **99**, 3747; (c) C. D. Ritchie, *Pure Appl. Chem.*, 1978, **50**, 1281.

[2] E. A. Hill and W. J. Mueller, *Tetrahedron Letters*, 1968, 2564.

[3] (a) C. A. Bunton and S. K. Huang, *J. Amer. Chem. Soc.*, 1972, **94**, 3536; 1974, **96**, 515; (b) C. A. Bunton, S. K. Huang, and C. H. Paik, *ibid.*, 1975, **97**, 6262; (c) *Tetrahedron Letters*, 1976, 1445.

[4] 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; J. N. Ride, P. A. H. Wyatt, and Z. M. Zochowski, *ibid.*, 1974, 1188.

[5] (a) K. Hillier, J. M. W. Scott, D. J. Barnes, and F. J. P. Steele, *Canad. J. Chem.*, 1976, **54**, 3312; (b) S. H. Morris, J. M. W. Scott, and F. Steele, *ibid.*, 1977, **55**, 686.

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

[7] A. Pross, *J. Amer. Chem. Soc.*, 1976, **98**, 776, 4692; *Adv. Phys. Org. Chem.*, 1976, **14**, 69.

[8] C. A. Bunton, N. Carrasco, and W. E. Watts, *J.C.S. Perkin II*, 1979, 1267.

[9] (a) C. A. Bunton, N. Carrasco, and W. E. Watts, *J. Organometallic Chem.*, 1977, **131**, C21; *J.C.S. Chem. Comm*, 1977, 529; (b) *ibid.*, 1979, 283; (c) C. A. Bunton and W. E. Watts, *Tetrahedron Letters*, 1977, 2049; C. A. Bunton, N. Carrasco, and W. E. Watts, *ibid.*, 1980, **21**, 407; (d) C. A. Bunton, W. Crawford, and W. E. Watts, *ibid.*, 1977, 3755; W. Crawford and W. E. Watts, *J. Organometallic Chem.*, 1980, **185**, 443; C. A. Bunton, W. Crawford, N. Cully, and W. E. Watts, *J.C.S. Perkin I*, 1980, 2213.

[10] (a) M. Cais, *Organometallic Chem. Rev.*, 1966, **1**, 435; (b) W. E. Watts, *J. Organometallic Chem. Library*, 1979, **7**, 399.

[11] E. A. Hill and R. Wiesner, *J. Amer. Chem. Soc.*, 1969, **91**, 509; A. N. Nesmeyanov, L. I. Kazakova, M. D. Reshetova, L. A. Kazitsina, and E. G. Perevalova, *Izvest. Akad. Nauk S.S.S.R., Ser. Khim.*, 1970, 2804; E. A. Hill, *J. Organometallic Chem.*, 1970, **24**, 457; J. Tirouflet, E. Laviron, C. Moïse, and Y. Mugnier, *ibid.*, 1973, **50**, 241; G. Cerichelli, B. Floris, and G. Ortaggi, *ibid.*, 1974, **78**, 241; T. D. Turbitt and W. E. Watts, *J.C.S. Perkin II*, 1974, 185; S. Allenmark, K. Kalén, and A. Sandblom, *Chem. Scripta*, 1975, **7**, 97.

[12] See I. I. Schuster, A. K. Colter, and R. J. Kurland, *J. Amer. Chem. Soc.*, 1968, **90**, 4679; V. V. Negrebetskii, N. N. Bychkov,

A. I. Bokanov, and B. I. Stepanov, *J. Gen. Chem. U.S.S.R.*, 1978, **48**, 2166.

[13] V. J. Shiner in ' Isotope Effects in Chemical Reactions,' eds. C. J. Collins and N. S. Bowman, van Nostrand Reinhold, New York, 1970, ch. 2; E. H. Cordes and H. G. Bull, *Chem. Rev.*, 1974, **74**, 581.

[14] F. Banoo and R. Stewart, *Canad. J. Chem.*, 1969, **47**, 3199.

[15] S. Uršić and S. Ašperger, *J. Inorg. Nuclear Chem.*, 1979, **41**, 1329.

[16] S. Braun, T. S. Abram, and W. E. Watts, *J. Organometallic Chem.*, 1975, **97**, 429.

[17] T. C. Bruice and J. E. Dixon, *J. Amer. Chem. Soc.*, 1971, **93**, 3248.

[18] M. M. Kreevoy in ' Isotopes in Organic Chemistry,' eds. E. Buncel and C. C. Lee, Elsevier, Amsterdam, vol. 2, ch. 1; *cf.* C. A. Bunton and V. J. Shiner, *J. Amer. Chem. Soc.*, 1961, **73**, 3214.

[19] W. P. Jencks, *Chem. Rev.*, 1976, **9**, 425; R. A. More O'Ferrall, *J. Chem. Soc. (B)*, 1970, 274.

[20] C. A. Bunton and R. H. DeWolfe, *J. Org. Chem.*, 1965, **30**, 1371.

[21] T. H. Fife, *Accounts Chem. Res.*, 1972, **5**, 264.

[22] D. J. Creighton, J. Hajdu, G. Mooser, and D. S. Sigman, *J. Amer. Chem. Soc.*, 1973, **95**, 6855; J. J. Steffens and D. M. Chipman, *ibid.*, 1971, **93**, 6694.

[23] M. Cais, P. Ashkenazi, S. Dani, and J. Gottlieb, *J. Organometallic Chem.*, 1976, **122**, 403; 1977, **124**, 49.

[24] R. Gleiter and R. Seeger, *Helv. Chim. Acta*, 1971, **54**, 1217; see also R. Hoffmann and P. Hofmann, *J. Amer. Chem. Soc.*, 1976, **98**, 598.

[25] (a) S. Lupan, M. Kapon, M. Cais, and F. H. Herbstein, *Angew. Chem. Internat. Edn.*, 1972, **11**, 1025; M. Cais, S. Dani, F. H. Herbstein, and M. Kapon, *J. Amer. Chem. Soc.*, 1978, **100**, 5554; (b) R. L. Sime and R. J. Sime, *ibid.*, 1974, **96**, 892; U. Behrens, *J. Organometallic Chem.*, 1979, **182**, 89.

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

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

[28] N. Weliky and E. S. Gould, *J. Amer. Chem. Soc.*, 1957, **79**, 2742.