Nucleophilic Addition to Ferrocenyl-stabilized Carbocations: a Test of the Generality of the N_+-Correlation

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Summary Rate constants for reactions of p-$MeOC_6H_4$-C^+HFc (**1**) (Fc = ferrocenyl) in water and of (**1**) and Fc_2C^+H in water–acetonitrile with neutral and anionic nucleophiles have been measured; the data are only approximately correlated by the Ritchie N_+-relationship and comparison of the rate constants for reactions of (**1**) and of $(p\text{-}MeOC_6H_4)_3C^+$ in water with nucleophiles suggests that reactions of the latter with bulky amines are subject to steric hindrance.

FACTORS affecting the rates of nucleophilic additions to pre-formed organic cations have been studied extensively.[1–3] Ritchie showed[1] that the reactivities towards such cations of a wide range of nucleophiles followed the expression $\log(k/k_0) = N_+$ where k and k_0 are, respectively, the rate constants for reactions of a cation with a given nucleophile and with water, and N_+ is a parameter characteristic of the nucleophilic system and independent of the cation.‡ Since the N_+-correlation implicitly questions the validity of the Hammond postulate and the reactivity–selectivity principle

TABLE

Rate constants for nucleophilic addition[a]

		Cation			
Nucleophile	N_+[b]	(**1**)[c]	(**1**)[d]	(**2**)[c,e]	(**3**)[d]
H_2O	0	41·0	58·0	12·0	$2{\cdot}6 \times 10^{-2}$
HO^-	4·75	$3{\cdot}0 \times 10^{4}$	$4{\cdot}3 \times 10^{4}$	$6{\cdot}7 \times 10^{3}$	$4{\cdot}25 \times 10^{2}$
CN^-	3·67	$9{\cdot}1 \times 10^{3}$		$2{\cdot}7 \times 10^{3}$	
N_3^-	7·6	$7{\cdot}4 \times 10^{6}$		$5{\cdot}0 \times 10^{6}$	$2{\cdot}7 \times 10^{4}$
BH_4^-	5·18[f]	$1{\cdot}5 \times 10^{6}$		$1{\cdot}3 \times 10^{6}$	$1{\cdot}8 \times 10^{3}$
BH_3CN^-	4·1[f]	$7{\cdot}4 \times 10^{3}$	$6{\cdot}4 \times 10^{4}$	$9{\cdot}0 \times 10^{3}$	62·0
N_2H_4	5·65	$3{\cdot}8 \times 10^{5}$		$3{\cdot}2 \times 10^{5}$	$3{\cdot}8 \times 10^{2}$
$MeONH_2$	3·88	$1{\cdot}2 \times 10^{4}$	*ca.* 5×10^{5}		
Imidazole	3·65	$9{\cdot}6 \times 10^{3}$	$7{\cdot}5 \times 10^{4}$	$5{\cdot}6 \times 10^{2}$	26·0
BDHNA[g]	5·1[f]	$1{\cdot}45 \times 10^{5}$		$2{\cdot}1 \times 10^{5}$	47·0

[a] Rate constants are in l mol^{-1} s^{-1} except for the water reaction (s^{-1}). [b] Values from ref. 1 unless indicated otherwise. [c] In water at 25·0 °C. [d] In water–acetonitrile (1 : 1 w/w) at 25·0 °C. [e] Ref. 2. [f] Given by $\log(k/k_0)$ for reactions of Malachite Green (ref. 2b). [g] 1-Benzyldihydronicotinamide.

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‡ Deviations from this relationship are usually < 0·5 log unit (ref. 1).

in relation to cation–nucleophile combinations, we have investigated its applicability to reactions of ferrocenyl-stabilized carbocations. Such cations, which collapse by preferential addition from the *exo*-side of their fulvene-like ligand,[4a] provide a good test system since wide structural variations can be exploited[4,5] and $\mathrm{C^+}$-substituent effects upon cation stability are attenuated compared with those for triarylmethyl cations.[5,6]

We have determined second-order rate constants in water and in water–acetonitrile for nucleophilic additions to $p\text{-}\mathrm{MeOC_6H_4C^+HFc}$ (**1**) (Fc = ferrocenyl) using methods previously described[2] for reactions of $(p\text{-}\mathrm{MeOC_6H_4})_3\mathrm{C^+}$ (**2**). Selected values are in the Table. Rate constants were also measured for nucleophilic additions to $\mathrm{Fc_2C^+H}$ (**3**) in water–acetonitrile.[§] The $\mathrm{p}K_{\mathrm{R}+}$ values for these cations in this mixed solvent (1 : 1 w/w) are 0·47 (**1**), 0·08 (**2**), and 3·20 (**3**); the corresponding values in water are 0·75—0·9 units more positive.[6] As is generally the case, the rates of nucleophilic additions do not closely follow $K_{\mathrm{R}+}$. The nucleophiles included water, ammonia, several anions, and anionic hydride-donors, and primary and secondary amines.

Values of N_+ have not been assigned to all the nucleophilic systems used but, where these are available,[1,2b] a plot of log k against N_+ for reactions of (**1**) in water is approximately linear with a slope of 0·7; the log k_0 value ($\mathrm{H_2O}$) lies on the line but log k for morpholine is too large by *ca.* one unit. Alternatively, the log k values can be fitted approximately to N_+ with unit slope provided that the value for water is excluded. Ritchie has noted[1] that rate constants for addition of water and hydroxide ion often deviate from an N_+-correlation. However, a plot of log (k/k_0) for nucleophilic attack on (**1**) in water against the corresponding values for (**2**) is linear with unit slope (Figure) with only the points for bulky amines deviating markedly. The deviation is very large for t-butylamine suggesting that steric hindrance to its attack on the tertiary cation (**2**) is much larger than on the secondary cation (**1**). Reactions of tertiary amines with ferrocenyl-carbocations in aprotic solvents involve electron transfer,[7] but primary and secondary amines add as nucleophiles[4b,7] and we saw no evidence for reactions other than nucleophilic addition.

The success of the N_+-correlation has led to the suggestion[1] that there are no extensive covalent interactions in the transition state for nucleophilic addition to carbocations, which is difficult to reconcile with our evidence for steric hindrance of addition to (**2**). Furthermore, an earlier observation[2] of general base catalysis points to extensive covalent interactions in the transition state.[¶] A model has been proposed[8] which interprets the N_+-correlation in terms of an advanced transition state with significant desolvation of the electrophile. Our experiments with the sterically hindered amines suggest that steric bulk at the cation centre may introduce hitherto unrecognised selectivity into any reactivity scale based on N_+.

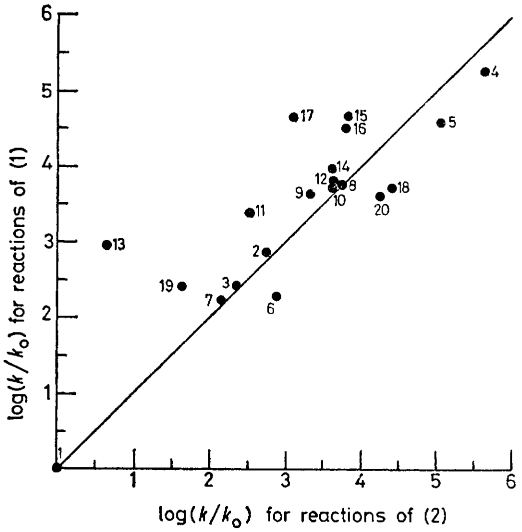

FIGURE. The line is drawn arbitrarily with unit slope and to include the value for water. The nucleophiles (in water) are $\mathrm{H_2O}$ (1), $\mathrm{HO^-}$ (2), $\mathrm{CN^-}$ (3), $\mathrm{N_3^-}$ (4), $\mathrm{BH_4^-}$ (5), $\mathrm{BH_3CN^-}$ (6), $\mathrm{NH_3}$ (7), $\mathrm{MeNH_2}$ (8), $\mathrm{EtNH_2}$ (9), $\mathrm{Pr^nNH_2}$ (10), $\mathrm{Pr^iNH_2}$ (11), $\mathrm{Bu^nNH_2}$ (12), $\mathrm{Bu^tNH_2}$ (13), $\mathrm{PhCH_2NH_2}$ (14), $\mathrm{Me_2NH}$ (15), piperidine (16), morpholine (17), $\mathrm{N_2H_4}$ (18), imidazole (19), and 1-benzyldihydronicotinamide (20).

In addition we note that, except for steric effects, nucleophilicities (relative to water) are almost identical for the cations (**1**) and (**2**), which are of very similar reactivities but whose nucleophilicities only approximately follow the N_+-scale. Both these observations suggest that the reactivity–selectivity principle cannot be wholly neglected. Nonetheless, the general applicability of the N_+-correlation is remarkable and our rate constants for reactions of (**3**) in water–acetonitrile follow a reactivity pattern similar to that for the other cations in water (Table); some of the differences can be rationalized in terms of differences in solvation.

We thank the National Science Foundation for support and the Leverhulme Trust for a research fellowship (to W.E.W.).

(*Received*, 28*th April* 1977; *Com.* 407.)

[§] Neutral products derived from this cation are sparingly soluble in water.

[¶] General bases catalyse reactions of some ferrocenyl-carbocations with water, but we found no catalysis of reactions with amines.

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