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Preliminary communication

RATES OF REACTIONS OF FERROCENYLCARBOCATIONS WITH WATER

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Summary

Secondary ferrocenylcarbenium ions ($Fc\overset{+}{C}HAr$) are much more reactive towards water than tertiary analogues ($Fc\overset{+}{C}Ar_2$ or $Fc\overset{+}{C}RAr$) and, in acid, are formed more rapidly from alcohols. The cations are stabilized by p-OMe and, when R = t-Bu or 1-adamantyl, the acid conversion of alcohol into cation is retarded.

As part of a study of the rates of reactions of metal-stabilized carbocations with nucleophiles, we have investigated the spontaneous reactions with water of the ferrocenylcarbenium ions Ia-i which were prepared both as isolable tetrafluoroborate salts and, in solution, as trifluoroacetate salts by dissolution of the corresponding alcohols in CF_3CO_2H. The first-order rate constants, k_f, for addition of water to the aryl- (Ia,b), diaryl- (Ic-e), and aryl/alkyl- (If-i) substituted cations are in the Table together with the second-order rate constants,

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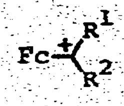

(I)

(a) $R^1 = H$, $R^2 = Ph$
(b) $R^1 = H$, $R^2 = An$
(c) $R^1 = R^2 = Ph$
(d) $R^1 = Ph$, $R^2 = An$
(e) $R^1 = R^2 = An$
(f) $R^1 = Ph$, $R^2 = Bu$
(g) $R^1 = An$, $R^2 = Bu$
(h) $R^1 = Ph$, $R^2 = Ad$
(i) $R^1 = An$, $R^2 = Ad$

(Fc = ferrocenyl; An = p-anisyl; Bu = t-butyl; Ad = 1-adamantyl)

k_r, for reaction of the alcohols with H_3O^+ and the pK_R+ values which are for water as the standard state. These cations cannot deprotonate and reaction with water cleanly gives alcohol.*

Because of insolubility, the pK_R+ values for the tertiary carbocations Ic-i could not be measured directly in aqueous acid. However, using pK_R+ values measured conventionally [1] for the secondary carbocations Ia,b in aqueous HCl, and $\log([R^+]/[ROH])$ values determined spectrophotometrically in H_2O:MeCN (1:1 w/w) containing H_2SO_4, an $H_R^{Fc}(H_2O:MeCN)$ acidity scale was devised following established methods [1]. This scale is linearly related to the H_R scale [2] for aqueous H_2SO_4 (0.5-4.0 M) :

$$H_R^{Fc}(H_2O:MeCN) = 1.26H_R + 1.34$$

For the tertiary carbocations Ic-i in $H_2SO_4:H_2O:MeCN$, plots of $\log([R^+]/[ROH])$ vs. $H_R^{Fc}(H_2O:MeCN)$ were linear with slopes 0.97-1.02. The pK_R+ values for $H_2SO_4:H_2O:MeCN$ are ca. 0.9 unit more negative than those for water as the standard state which are in the Table. As noted earlier [3], these tertiary carbocations are unstable in acid, decomposing with liberation of the fulvene ligand. For pK_R+ determinations, the changing absorbances of such solutions were extrapolated back to the time of carbocation generation.

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* Study of the rates of reactions of deprotonatable ferrocenylcarbenium ions is complicated by cation + alkene coupling which generates a new, relatively unreactive "dimeric" cation; e.g. $\text{Fc}\overset{+}{\text{C}}\text{MePh} \rightarrow \text{Fc}\overset{+}{\text{C}}\text{PhCH}_2\text{CMePhFc}$.

Table Rate and Equilibrium Constants[a]

Cation	λ_{max}/nm	H_2O:MeCN		H_2O		
		k_f/s^{-1}	$k_r/M^{-1}s^{-1}$	k_f/s^{-1}	$k_r/M^{-1}s^{-1}$	pK_{R^+}
Ia	325	62.[b]	15.[b]	44.[c]	135.[c]	0.49
Ib	360	58.[b]	172.[b]	41.[d]	960.[d]	1.37
Ic	355	0.90	0.60			0.72
Id	440	0.46	2.19			1.58
Ie	430	0.20	15.9			2.80
If	345	0.58	0.0036			-1.31
Ig	370	0.86	0.014			-0.88
Ih	342	0.24	0.0052			-0.76
Ii	375	0.32	0.0092			-0.64
An_3C^+	483	7.4[e]	8.9[e]	12.[f]	76.[f]	0.82[f]

[a] At 25.0°C [b] 0.125 M H_2SO_4 [c] 0.0125 M HCl [d] 0.125 M HCl
[e] 0.25 M H_2SO_4 [f] Ref. [4]

Reactions of Ia,b with water were followed at the wavelengths indicated (Table) in H_2O and in H_2O:MeCN using a Durrum stopped-flow spectrophotometer. Typically, an equilibrium mixture of cation and alcohol in HCl:H_2O or H_2SO_4:H_2O:MeCN was added to H_2O or H_2O:MeCN so that the observed first-order rate constant was the sum of the forward and reverse rate constants ($k_f + k_r[H^+]$) which were separated using the appropriate pK_{R^+} value. Reactions of Ic-i with water were followed in H_2O:MeCN using a Gilford spectrophotometer by adding a solution (ca. 2μl) of the tetrafluoroborate in MeCN or $(CH_2Cl)_2$ to the reaction solvent (ca. 3ml). Identical k_f rate constants were obtained by adding a solution of the trifluoroacetate in CF_3CO_2H.

Assuming that differences between the ground-state energies of the alcohols in aqueous media are relatively insignificant, the pK_{R^+} values for the mono- and di-aryl species Ia-e show that there is considerable stabilization of the carbocation by $\overset{+}{C}$-aryl groups, e.g. p-anisyl is almost as effective here as in the triarylmethyl system [4]. As shown by the pK_{R^+} values for If-i, however, introduction of a t-butyl or 1-adamantyl group into the secondary carbocations Ia,b markedly destabilizes the cation, despite the +I effect. We attribute this anomaly to steric hindrance by the bulky alkyl groups to coplanarity of the $C_5H_4C^+$ and aryl moieties.

The k_f values show a different pattern. As expected, the secondary carbocations (Ia,b) are much more reactive than the tertiary (Ic-i). However, the bulky alkyl groups in If-i which destabilize the ions also reduce k_f, showing that steric hindrance to nucleophilic addition of water overcomes any rate enhancement due to steric inhibition of resonance. A p-methoxy group reduces k_f more in the tertiary cations Ic-e than in the secondary Ia,b. Recent ^{13}C-NMR studies [5] have suggested that there is significantly greater charge concentration at the formal $\overset{+}{C}$-centre of tertiary as compared with secondary ferrocenylcarbocations which may account for the observed trends. For the aryl/alkyl systems If-i, the modest rate enhancements by the p-methoxy group further indicate steric suppression of π-conjugation between the $\overset{+}{C}$-centre and the aryl group.

Substituent effects are much larger on k_r than on k_f. A p-methoxy group markedly increases k_r for the mono- and di-aryl systems Ia-e but reduces k_r for the aryl/alkyl systems If-i, presumably reflecting steric hindrance to alcohol heterolysis. Bulky substituents reduce k_r by forcing the alcohol into an unfavourable conformation for heterolysis (nucleophiles add and depart preferentially from the exo-direction), and by inhibiting resonance stabilization of the transition state. These effects also explain the higher reactivities of the secondary over the tertiary alcohols.

The observed dependence of k_f and k_r on structure accords with a carbocation-like transition state, a situation similar to that for nucleophilic additions to triarylmethyl cations [4]. Consistently, the small deuterium kinetic solvent isotope effects for addition of water in $H_2O(D_2O)$:MeCN to the cations Ic-i ($k_f^{H_2O}/k_f^{D_2O}$ = 1.10-1.23) are very similar to that [6] for addition of water to the tri-p-anisylmethyl cation ($k_f^{H_2O}/k_f^{D_2O}$ = 1.2).

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