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Preliminary communication

A MECHANISTIC STUDY OF THE FRAGMENTATION OF FERROCENYLDIARYLMETHYLIUM IONS IN AQUEOUS ACIDIC ACETONITRILE

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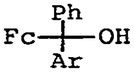
Summary

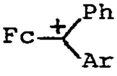
Ferrocenylcarbocations of the type $Fc\overset{+}{C}ArAr'$ (Ar,Ar' = aryl groups) decompose in aqueous acidic acetonitrile liberating the 6,6-diarylpentafulvene ligand. The mechanism of the reaction has been studied by product analysis and by kinetic measurements.

Although secondary ferrocenylcarbocations of the type $Fc\overset{+}{C}HAr$ (Ar = aryl or ferrocenyl) are stable in aqueous acidic solutions in which they exist in equilibrium with the corresponding alcohols FcCHArOH [1,2], tertiary diaryl analogues $Fc\overset{+}{C}ArAr'$ decompose in such media with liberation of the 6,6-diarylpentafulvene ligand. Although reactions of this type were first reported [3] in 1965 and have been noted subsequently as complicating side-reactions during pK_{R^+} measurements [1,2], the mechanism of the reaction has not been studied.

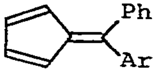


$Fc-\underset{Ar}{\overset{Ph}{C}}-OH$

(I)



(II)



(III)

(a) Ar = Ph
(b) Ar = p-anisyl

The blue ferrocenyldiphenylmethylium ion (IIa) was generated quantitatively when the alcohol (Ia) was dissolved in conc. H_2SO_4 or

CF_3CO_2H and was fairly stable in these solvents; the electronic and ^1H n.m.r. spectra[*] of these solutions showed little deterioration with time over several hours. Furthermore, BF_4^- and ClO_4^- salts of (IIa), prepared by Allenmark's method [4], were stable in solution in anhydrous MeCN. Addition of NaOH/H_2O and NaOMe/MeOH to these MeCN solutions gave quantitative yields of the addition products (Ia) and $FcCPh_2OMe$ respectively.

However, in equilibrium with the precursor (Ia) in H_2O:MeCN (1:1 w/w) containing HCl or H_2SO_4, the cation (IIa) decomposed within a few hours giving a solution from which the fulvene (IIIa) was isolated and identified by comparison with an authentic sample prepared by base-catalysed condensation of benzophenone and cyclopentadiene. The green anisylferrocenylphenylmethylium ion (IIb) was also unstable in this solvent system, decomposing similarly with formation of the fulvene (IIIb). In these reactions, the expelled $CpFe^+$ fragment broke down further to inorganic iron salt(s) and, presumably, cyclopentadiene. No evidence for the formation of Cp_2Fe, Cp_2Fe^+, or $Cp\overset{+}{F}e(NCMe)_3$ was found. Attempts to trap this fragment with π-rich ligands were unsuccessful. Thus, when (IIa) was allowed to decompose to (IIIa) in the presence of mesitylene or 6,6-dimethylpentafulvene, no trace of the known complex $[CpFe(mesitylene)]^+$ [5] or of neutral products derived from $Fc\overset{+}{C}Me_2$ [6] respectively was found in the product mixtures.

These experiments establish that the cations (IIa,b) fragment, releasing the fulvene ligand (IIIa,b), in aqueous acidic media in which repeated reversible formation from the alcohol precursors (Ia,b) occurs. Kinetic studies were carried out in order to investigate the effect of change in acid strength. Following addition of (Ia) in EtOH (ca. 50μl) to H_2O:MeCN (1:1 w/w; ca. 3ml) containing H_2SO_4 at predet-

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[*] λ_{max} (H_2SO_4) nm/logε : 258/4.05, 360/4.06, and 550/3.35.
^1H n.m.r. (CF_3CO_2H) τ: 2.0-2.8 (m, Ph), 3.4 and 4.6 (2t, C_5H_4), and 5.1 (s, C_5H_5).

ermined concentrations at 27.5°C, the progress of the reactions was followed spectroscopically by monitoring the rate of growth of the fulvene absorption at 325 nm. The reactions obeyed a first-order kinetic law through at least four half-lives and the calculated pseudo-first-order rate constants (k_{obs}) were found to be linearly dependent upon the concentration of acid present in solution (see Table).

In kinetic terms, the reaction can be depicted as follows:

$$H^+ + (I) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2O + (II) \xrightarrow{k_2} (III)$$

Since $k_2 \ll k_{-1}$ (see later), the kinetic scheme approximates to a system in which fulvene (III) results by depletion of an alcohol (I)/ cation (II) mixture whose composition is maintained close to an equilibrium value through the reaction. Assuming such pre-equilibrium conditions, $k_{obs} = [H^+]k_1k_2/k_{-1} = [H^+]k_2/K_{R^+}$, whence $k_2 = k_{obs}K_{R^+}/[H^+]$. The equilibrium constant ($K_{R^+} = 1.51M$) has been measured [2] for the interconversion (IIa) $\rightleftharpoons$ (Ia) in the H_2O:MeCN:H_2SO_4 solvent system used for the rate measurements and k_2 values, calculated from the earlier expression, are in the Table. Through the range of acid concentrations used, k_2 for the cation (IIa) → fulvene (IIIa) reaction is unaffected by change in acid concentration. Furthermore, since $k_{-1} \approx 35k_2$,* the cation (IIa) returns to alcohol (Ia) at a rate much faster than that for dissociation into fulvene (IIIa), in accord with the earlier assumption of pre-equilibrium conditions.

We have also carried out some preliminary rate experiments to investigate substituent effects. For example, a p-methoxy phenyl substituent causes modest reductions in the rate constants k_{-1} and k_2 (with $k_2 \ll k_{-1}$ as before) for addition and fragmentation reactions respectively of the cation (IIb) ($K_{R^+} = 0.21M$ [2]) compared with corresponding values for (IIa). Finally, it appears that the apparent

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* The rate constant ($k_{-1} = 0.90\ s^{-1}$) for addition of water to (IIa) in H_2O:MeCN is only modestly depressed in the presence of H_2SO_4 at concentrations $\leqslant 0.50M$ [7].

Table. Rate constants for (Ia) $\rightleftharpoons$ (IIa) $\longrightarrow$ (IIIa)[a]

$[H_2SO_4]$[b] M	k_{obs}[c] s^{-1}	$k_{obs}/[H_2SO_4]$ $s^{-1}M^{-1}$	k_2[d] s^{-1}
0.10	1.65×10^{-3}	1.65×10^{-2}	2.49×10^{-2}
0.20	3.33×10^{-3}	1.67×10^{-2}	2.51×10^{-2}
0.30	5.21×10^{-3}	1.74×10^{-2}	2.62×10^{-2}
0.40	6.83×10^{-3}	1.71×10^{-2}	2.58×10^{-2}
0.50	8.56×10^{-3}	1.71×10^{-2}	2.59×10^{-2}

[a] At 27.5°C. [b] In H_2O:MeCN (1:1 w/w). [c] Average values.

[d] Assuming $k_2 = k_{obs}K_{R^+}/[H^+] = k_{obs}K_{R^+}/[H_2SO_4]$.

stability towards fragmentation in aqueous acidic media of cations of the type $Fc\overset{+}{C}HAr$ may be a consequence of very much larger k_{-1}/k_2 partitioning ratios compared with those for cations of the type (II).

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