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STABLE CARBOCATIONS

XX *. A KINETIC STUDY OF THE S_N1 HYDROLYSIS OF ARYL(FERROCENYL)METHYL ACETATES *

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Summary

Rate constants (k) for solvolysis of a series of acetates, p-$RC_6H_4CH(OAc)Fc$, in aqueous acetone have been determined. The log k_{rel} values correlate linearly with Hammett σ^+ substituent constants (ρ = —1.39) and with pK_{R^+} values for the intermediate ferrocenyl-stabilised carbocations, whose ^1H NMR spectra have been recorded. The mechanistic significance of the rate data is discussed.

Introduction

Following the report [2] in 1959 that (1-acetoxyalkyl)ferrocenes, FcCH(OAc)R, undergo exceptionally fast S_N1 hydrolysis in aqueous solutions, the kinetics of solvolysis of a wide range of ferrocenyl substrates have been measured by several groups in attempts to elucidate the source of the rate-accelerating effect of the ferrocenyl group and the related problem of the structure of the intermediate 1-ferrocenylalkyl cations, $Fc\overset{+}{C}HR$. A recent review of these and related studies has been published [3].

It is clear from this work that the rates of S_N1 solvolysis of substrates of the type FcCH(X)R are sensitive to a number of factors. Thus, steric and/or conformational constraints which hinder the preferred (anchimerically assisted) *exo*-departure of the leaving group (X^-) cause often large rate retardations [3—6]. Rates are also sensitive to the presence of substituents in the ferrocenyl group. For example, the rate constant for hydrolysis of FcCH(OAc)Me in aqueous acetone is increased ca. twofold upon introduction of a 1′-methyl group and reduced ca. 60-fold in the presence of a 1′-carbomethoxy substituent [7].

For substrates of the type FcCH(X)Ar, available kinetic data suggest that

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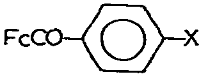
* For Part XIX, see ref. 1.

the rates of S_N1 heterolysis are only moderately sensitive to aryl substituent effects. For example, introduction of a *p*-methoxy substituent has been reported to cause only a ca. 10-fold increase in the rate constants for hydrolysis of FcCH(OAc)Ph [8,9] and for acid-promoted heterolysis of FcCH(OH)Ph [6a]. In order to investigate more fully this substituent effect, we have measured the rates of hydrolysis in aqueous acetone of a series of esters of the type III with a view to determining the Hammett ρ-value for the reaction.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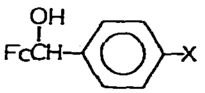
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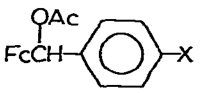
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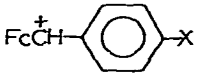
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a; X = H b; X = Me c; X = OMe d; X = CF_3

Discussion

The required acetates (IIIa—IIId) were prepared by a conventional sequence of reactions. Friedel—Crafts acylation of ferrocene with the aroyl chlorides in CH_2Cl_2 in the presence of Al_2Cl_6 gave the ketones (Ia—Id) which, on treatment with $LiAlH_4$ in ether followed by hydrolysis, underwent quantitative reduction to the corresponding alcohols (IIa—IId). The acetates (IIIa—IIId) were then obtained by esterification of these alcohols using acetic anhydride in pyridine.

The rates of solvolysis of the acetates (IIIa, IIIb, IIId) in 80% acetone/water were determined by a conventional titrimetric aliquot-sampling method by which the rate of liberation of acetic acid was measured. In order to obtain experimentally convenient rates of reaction, the solvolysis of the least reactive ester (IIId) was followed at 10°C and that of the much more reactive *p*-tolyl substrate (IIIb) at 0°C. The rate of reaction of the parent unsubstituted ester (IIIa) was determined at both of these temperatures to permit proper comparison of relative rates. The rate of solvolysis of the very reactive *p*-anisyl substrate (IIIc) in the same solvent was followed at 0°C using an automatic titrator pH-stat assembly. The calculated first-order rate constants (k) and relative rate constants (k_{rel}) are in Table 1 which also includes for comparison the corresponding rate constant for 1-ferrocenylmethyl acetate, which was determined earlier [4,6b].

Rates of solvolysis in aqueous acetone of a similar series of esters, viz. FcCH(OAc)Me, (IIIa—IIIc), and (III; X = CO_2Me), have apparently been measured previously by Belanic-Lipovac and Cais [9] but, to our knowledge, a report of this study giving experimental conditions and methods has not been published. Comparison of our data with the relative rate constants cited in the review article by Cais [8] shows a similar trend in ester reactivity although there are substantial differences in the magnitudes of some of the k_{rel} values (see Table 1).

The observed *p*-aryl substituent effect on solvolysis rate is in accord with an S_N1 mechanism in which the transition state for acetate heterolysis (i.e. carbocation formation) is stabilised by electron-donating substituents (*p*-Me and *p*-OMe) and destabilised by electron-withdrawal (*p*-CF_3). However, the magnitude of these effects is much smaller than that observed for S_N1 solvolysis

TABLE 1

RATE AND EQUILIBRIUM DATA

Substrate	T (°C) [a]	$10^5 k$ (s^{-1}) [b]	k_{rel} [c]	σ^+ [d]	pK_{R^+} [e]
FcCH(OAc)Me	0	0.497 [f]	0.067 (0.26)		−0.66
IIIa	0 10	7.41 18.4	1.00	0.00	+0.49
IIIb	0	16.0	2.16 (1.82)	−0.31	+0.80 [g]
IIIc	0	111.0	15.0 (9.5)	−0.78	+1.37
IIId	10	4.12	0.22	+0.52	

[a] ±0.2°C at 0°C; ±0.1°C at 10°C. [b] First-order rare constants for solvolysis of acetates in 80% acetone/water; this work unless indicated otherwise; values are the average of at least two kinetic runs; [c] Rate constants relative to the value for IIIa; values in parentheses are those cited in ref. 8. [d] Aryl σ^+ substituent constants, taken from ref. 21. [e] pK_{R^+} Values for carboration ⇌ alcohol equilibria in aqueous acidic solutions; best values from refs. 3 and 6a unless indicated otherwise. [f] Value from ref. 6b. [g] Unpublished result (W.E. Watts).

reactions of benzyl and benzhydryl derivatives. Thus, a Hammett plot of our log k_{rel} values against the σ^+ substituent constants gives a good linear correlation (correlation coefficient 0.994) with a derived ρ-value of −1.39 for the reaction. This may be compared with the much more negative ρ-values associated with S_N1 reactions of related series of arylalkyl substrates e.g. for solvolysis of compounds of the types $ArCMe_2Cl$ and Ar_2CHCl, ρ-values fall in the range −4.0 to −4.7 [10].

There are two factors which, perhaps cooperatively, may account for this diminished sensitivity of the ferrocenyl substrates. Firstly, since the pronounced electron-releasing capacity of the ferrocenyl group [3] greatly exceeds that of phenyl, aryl substituent effects upon the energy of the S_N1 transition states for solvolysis of the esters (III) would be attenuated. Secondly, in view of the much greater thermodynamic stability of ferrocenylalkylium ions (e.g. Fc$\overset{+}{C}$HPh; pK_{R^+} = +0.49 [6a]) than of benzylic analogues (e.g. $Ph_2\overset{+}{C}H$; pK_{R^+} = −13.3 [11]), heterolytic bond-breaking may be much less advanced in the transition states for solvolysis of esters of the type III compared with the situation which obtains for benzyl or benzhydryl analogues. Diminished carbocation character in the former, $[Fc(Ar)\overset{\delta+}{C}H\cdots\overset{\delta-}{O}Ac]^{\neq}$, would reduce the sensitivity towards aryl substituent effects [12]. However, recent work [13] on secondary kinetic isotope effects has provided evidence that the transition states for addition of anionic nucleophiles (e.g. HO^-, N_3^-) to ferrocenylalkyl cations (e.g. $Fc_2\overset{+}{C}H$) in aqueous solution resemble ion pairs with little covalent bonding.

A further indication of carbocation character in the transition states for solvolysis of 1-ferrocenylalkyl acetates is shown by the linear correlation we find between the log k_{rel} values for the acetates (IIIa—IIIc) and FcCH(OAc)Me and the pK_{R^+} values (Table 1) for the corresponding intermediate carbocations (IVa—IVc) and Fc$\overset{+}{C}$HMe; the slope of the log k_{rel}/pK_{R^+} plot is 1.14. Similar linear relationships with slopes close to unity have been found earlier for reactions of benzhydryl [14] and other ferrocenylalkyl [15] substrates.

TABLE 2

^{1}H NMR SPECTRA OF CARBOCATIONS [a]

Cation	Proton resonances [b] (τ-values)					
	(C_5H_5) [c]	$H_\alpha(C_5H_4)$	$H_\beta(C_5H_4)$	$\overset{+}{C}H$ [c]	Aryl	X [c]
IVa	5.12	4.4—4.5, 5.1—5.3	3.45—3.6, 3.65—3.8	1.98	2.0—2.5	
IVb	5.26	4.5—4.65, 5.25—5.4	3.6—3.75, 3.85—4.0	1.95	2.2—2.45, 2.45—2.8 [d]	7.67
IVc	5.20	4.35—4.5, 5.1—5.25	3.5—3.7, 3.75—3.9	1.70	1.9—2.15, 2.7—2.85 [d]	6.00
IVd	5.02	4.4—4.55, 5.1—5.25	3.4—3.55, 3.55—3.7	1.97	2.07 [c]	

[a] For solutions in CF_3CO_2H with Me_4Si as internal reference, recorded using a Perkin—Elmer R12A spectrometer operating at 60 MHz. [b] Multiplets unless indicated otherwise. [c] Singlet resonance. [d] A_2B_2 pattern.

Finally, we have also recorded the ^{1}H NMR spectra of the cations (IVa—IVd) which were generated quantitatively upon dissolution of the alcohols (IIIa—IIId) in CF_3CO_2H. The features of these spectra (Table 2) are in accord with those established [3] for cations of this type and show that the chemical shifts of the ferrocenyl protons are rather insensitive to the nature of the aryl group.

Experimental

For general remarks, see Part XII [16]. All new compounds prepared gave satisfactory elemental analysis, and ^{1}H NMR and IR spectra were in accord with the structures assigned.

Preparation of ketones

The ketones (Ia—Id) were prepared from ferrocene according to standard procedures [17] using the appropriate aroyl chlorides in CH_2Cl_2 containing a slight excess of Al_2Cl_6, and were purified by chromatography on alumina: Ia, m.p. 111—113°C (lit. [18] 111.5—112°C); Ib, m.p. 131—133°C (lit. [18] 132°C); Ic, m.p. 81—83°C (lit. [18] 82—83°C); Id, m.p. 159—161°C.

Preparation of alcohols

The alcohols IIa—IId were prepared by reduction of the ketones Ia—Id using $LiAlH_4$ in ether, followed by hydrolysis, and were purified by chromatography: IIa, m.p. 78—80°C (lit. [18] 80.3—80.5°C); IIb, m.p. 87—89°C (lit. [19] 88—89°C); IIc, m.p. 73—75°C (lit. [19] 72—74°C); IId, m.p. 70—72°C.

Preparation of acetates

The acetates IIIa—IIId were prepared by esterification of the alcohols IIa—IId using Ac_2O in dry pyridine, according to the reported procedure [6b], and were purified by recrystallisation from pentane solutions: IIIa, m.p. 78—80°C; IIIb, m.p. 69—71°C; IIIc, m.p. 73—75°C; IIId, m.p. 75—77°C.

Kinetic studies

The 80% acetone/water solvent used for the rate measurements was prepared as described previously [4]. Rate runs were conducted at selected temperatures (0 to 10°C) either by the standard aliquot-sampling titrimetric method [4] or by use of an automatic titrator pH-stat apparatus whose components and method of operation have been detailed previously [6b]. For each method, the progress of the reaction was followed by measuring the rate of formation of HOAc by titration with aq. NaOH solution. Duplicate runs gave good reproducibility. First-order rate constants were calculated conventionally [20] using a least-squares best-fit computer program; correlation coefficients better than 0.998 were found in all cases.

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References

1 N. Cully, W.D. Quail and W.E. Watts, J. Chem. Soc. Perkin II, (1979) 1148.
2 J.H. Richards and E.A. Hill, J. Amer. Chem. Soc., 81 (1959) 3484.
3 W.E. Watts, J. Organometal. Chem. Library, 7 (1979) 399.
4 E.A. Hill and J.H. Richards, J. Amer. Chem. Soc., 83 (1961) 3840 and 4216.
5 D.S. Trifan and R. Bacskai, Tetrahedron Lett., (1960) 1.
6 (a) C.A. Bunton, N. Carrasco and W.E. Watts, J. Organometal. Chem., 131 (1977) C21; J. Chem. Soc. Perkin II, in press; (b) N. Cully, J. Park and W.E. Watts, ibid., (1979) 947.
7 D.W. Hall, E.A. Hill and J.H. Richards, J. Amer. Chem. Soc., 90 (1968) 4972.
8 M. Cais, Organometal. Chem. Revs., 1 (1966) 435.
9 V. Belanic-Lipovac and M. Cais, unpublished results cited in ref. 8.
10 J.E. Lefflet and E. Grunwald, Rates and Equilibria of Organic Reactions, Wiley, New York, 1963, pp. 208—209.
11 N.C. Deno, J.J. Jaruzelski and A. Schriesheim, J. Amer. Chem. Soc., 77 (1955) 3044.
12 Cf. E.A. Hill and R. Wiesner, J. Amer. Chem. Soc., 91 (1969) 509.
13 C.A. Bunton, N. Carrasco and W.E. Watts, J. Chem. Soc. Chem. Commun., (1979) 283.
14 N.C. Deno and A. Schriesheim, J. Amer. Chem. Soc., 77 (1955) 3051.
15 G. Cerichelli, B. Floris and G. Ortaggi, J. Organometal. Chem., 78 (1974) 241.
16 T.D. Turbitt and W.E. Watts, J. Organometal. Chem., 46 (1972) 109.
17 T.D. Turbitt and W.E. Watts, J. Chem. Soc. Perkin II, (1974) 177.
18 M. Rosenblum, Chemistry of the Iron Group Metallocenes, Part 1, Interscience, New York, 1965.
19 M. Cais and A. Eisenstadt, J. Org. Chem., 30 (1965) 1148.
20 A.A. Frost and R.G. Pearson, Kinetics and Mechanism, 2nd ed. Wiley, New York, 1961.
21 E.M. Kosower, An Introduction to Physical Organic Chemistry, Wiley, New York, 1968, p. 49.