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Preliminary communication

Ferrocenylalkyl Carbocations. II. Contribution to the Problem of the Structure of Ferrocenylmethyl Carbocation

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In this communication, an unusually large secondary α-deuterium kinetic isotope effect for hydrolysis of the ferrocenylmethylquinolinium ion, that elucidates significantly the problem of the structure and manner in which stabilisation of the α-ferrocenylalkyl carbocations occurs, will be reported. This problem arises mainly from uncertainties as to whether some direct bonding between iron and the cationic center is of significance in the stabilisation of α-ferrocenylalkyl carbocations[1].

Hydrolysis of ferrocenylmethylquinolinium chloride was carried out at 25 °C. Rate constants for hydrolysis in water and 80 : 20 water-acetonitrile were determined spectrophotometrically. Results, together with corresponding α-deuterium kinetic isotope effects are given in Table I.

Some secondary α-deuterium kinetic isotope effects for C—N bond cleaveage in unimolecular solvolysis have been determined[2-4], (Table II) and only a few of them are similar in magnitude to the isotope effect reported here. The magnitude of a kinetic isotope effect is directly connected with the transition state structure, and variations in the transition state structure should result in variations in the isotope effect. Cordes et al. suggested[2] that very similar α-deuterium isotope effects obtained in inosine and adenosine hydrolysis, (first and second entry in Table II) originate from a C—N bond being largely or completely cleaved in the transition state. Similary, an α-deuterium isotope effect of ca. 1.24 per deuterium atom for hydrolysis of the ferrocenylmethylquinolinium ion in water clearly suggested that the $sp^3 \rightarrow sp^2$ rehybridization is nearly complete or complete on going from reactants to the transition state. Such a conclusion is supported if one considers the similarity in secondary α-deuterium kinetic isotope effects for C—O and C—N bond cleaveage[1,4]. Thus, an α-deuterium isotope effect of ca. 1.23 is usually considered to be near to the maximum expected for C—O bond cleaveage[5].

The present results for hydrolysis of the ferrocenylquinolinium ion in water strongly indicate that there is no significant bonding between iron and the α-cationic center in the transition state for hydrolysis, since such a participation of iron must result in an effect substantially smaller than the isotope effect observed[4,5]. Therefore, most of the models[6a] for α-ferrocenylalkyl carbocation which allow direct bonding between iron and α-carbon probably need to be

TABLE I

Rates of Hydrolysis of Ferrocenylmethylquinolinium Ion at 25 °C

Substrate[a]	Solvent	Rate constant[d,e] $10^4\ s^{-1}$	α-deuterium kinetic isotope effect
$FcCH_2Q^+$	Water[b]	0.658 ± 0.006	1.479 ± 0.024
$FcCD_2Q^+$		0.445 ± 0.006	
$FcCH_2Q^+$	Water-acetonitrile[c] 80 : 20 v/v	0.798 ± 0.020	1.237 ± 0.049
$FcCD_2Q^+$		0.645 ± 0.020	

[a] Fc = ferrocenyl, Q = quinolinium. Ferrocenylmethylquinolinium chloride was prepared from ferrocenylmethyl carbinol and quinolinium hydrochloride in acetonitrile. Corresponding deuterated substance was prepared analogously from deuterated carbinol (see ref. 1). M. p. 119—121 °C. Assay of $FcCH_2QCl$ 99% (by potentiometric titration of chloride). Log ε (in water) is 4.44(236 nm), 3.45(280 nm), 3.76(313 nm), 2.13(380 nm) and 2.47(443 nm). Spectra of solvolytic products in comparison with spectra of authentic samples (ferrocenylcarbinol and quinolinium hydrochloride) confirmed the structural assignement. When ferrocenylcarbinol in solvolysis mixture was (after 8 half-lives) oxidized with ferric perchlorate to the corresponding ferricenium product, comparison of absorbance at 627 nm with an authentic sample of oxidized carbinol indicated (within experimental error) that solvolysis of $FcCH_2Q^+$ gives quantitatively ferrocenylcarbinol.

[b] With 0.3% v/v acetonitrile added. Ionic strength of 0.5 was maintained with benzyltrimethylammonium chloride.

[c] Ionic strength 0.3, salt benzyltrimethylammonium chloride.

[d] Kinetics were measured spectrophotometrically, by following differences in absorbance at 456 nm. Individual rate constants were computed using an nonlinear regression analysis. Reported rate constants are the mean of four (hydrolysis in water) or eight (hydrolysis in water-acetonitrile) individual constants.

[e] Control experiments with added base (NaOH, amount equal to that of $FcCH_2Q^+$ substrate) or acid (10^{-3} M dm^{-3} HCl, fivefold acid over the substrate concentration) shows no significant rate depression or rate acceleration. In addition, almost identical rate constants were obtained from data for one half-live and assumed infinity absorbance (from spectra of quinoline hydrochloride and ferrocenylmethyl carbinol) and from data for four half-lives of solvolysis.

TABLE II

Kinetic Secondary α-Deuterium Isotope Effects for C—N Bond Cleaveage

Substrate	Leaving group	Kinetic α-deuterium Isotope effect	Ref.
inosine	hypoxantyne[a]	1.23 ± 0.02	2
adenosine	adenine[a]	1.229 ± 0.012	2
β-D-galactopyranosyl-4-bromoisoquinolinium ion	4-bromoisoquinoline	1.187 ± 0.046	3a
β-D-galactopyranosyliso-quinolinium ion	isoquinoline	1.17 ± 0.03	3b
β-D-galactopyranosylpyridinium ion	pyridine	1.13 ± 0.04[b]	3c
ferrocenylmethyl-trimethyl-ammonium ion	trimethylammine	1.06 ± 0.04[c,d]	4
ferrocenylmethylquino-linium ion	quinoline	1.479 ± 0.024[c]	this work

[a] purine base or protonated purine base

[b] At 100 °C, corresponding to one isotope effect of 1.16 at 25° C

[c] Isotope effects from two α-deuterium atoms

[d] at 80 °C

retracted. The ferrocenylmethyl carbocation was isolated as its tetrafluoroborate[7], but X-ray crystal analysis was performed only for some related secondary and tertiary carbocations[8]. These analyses offer some possibility for iron-cationic center interaction. Perhaps, there exist some differences between the transition state structure for solvolysis and the structure of α-ferrocenylalkyl carbocations in solid state and in solution.*

In 80 : 20 water-acetonitrile there is an essentially smaller α-deuterium isotope effect for solvolysis and somewhat greater rate of hydrolysis of an ferrocenylmethylquinolinium ion (cf. third and fourth entry in Table I). The small rate enhancement for hydrolysis is not surprising. This enhancement is expected for solvolysis of the cationic substrate when the dielectric constant of solvent is decreased, due to dispersal of charge in the transition state[9]. The magnitude of an α-deuterium isotope effect of ca. 1.12 (Table I) per deuterium atom is similar to that for hydrolysis of the β-D-galactopyranosylpyridinium ion (fifth entry in Table II), and to the α-deuterium kinetic isotope effect k_D/k_H calculated earlier for addition of pyridine to the ferrocenylmethyl carbocation in water[1].

It was observed[10] that addition of organic solvent to water markedly destabilised ferrocenylalkyl carbocations. On the other hand, Sinott and Jencks[11] reported that there is some specific but weak interaction with both the leaving group and the incoming solvent molecule in the transition state for solvolysis of α-D-glucopyranosylpyridinium ions. These interactions may be predominantly or entirely electrostatic.

There is probably, some interaction with solvent molecules in the transition state in the case of hydrolysis of ferrocenylmethylquinolinium ion in water-acetonitrile, which causes diminishing of the α-deuterium isotope effect. This problem will be further elaborated in an subsequent paper.

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* Recent Mössbauer spectroscopy analysis[6b] of α-ferrocenylalkyl carbocations seems to indicate some direct iron-cationic center interaction for FcC^+H_2 in frozen acidic solution.

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SAŽETAK

Ferocenilalkil karbokationi. II. Doprinos problemu strukture ferocenilmetil karbokationa

Stanko Uršić

Određen je sekundarni α-deuterijski kinetički izotopni efekt u solvolizi ferocenilmetilkinolinijeva iona i iznosi ca. 24% po atomu deuterija kod solvolize u vodi, te ca. 12% po D atomu kod solvolize u 80/20 vodi/acetonitrilu. Diskutirano je značenje tih rezultata u vezi sa strukturom ferocenilmetil karbokationa.