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Uršić, S.

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Ferrocenylalkyl Carbocations. Rates of Formation and Nucleophilic Additions to Ferrocenylmethyl Carbocation

S. Uršić

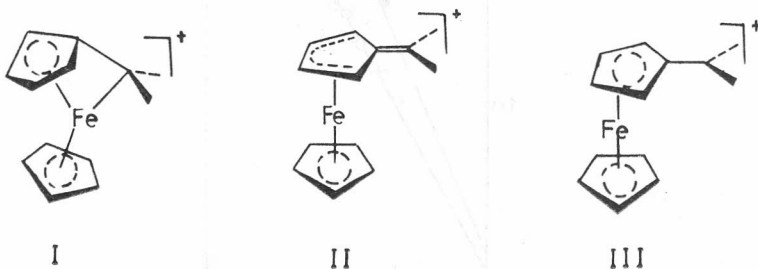
Faculty of Pharmacy and Biochemistry, University of Zagreb, 41000 Zagreb, Croatia, Yugoslavia

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Rate constants for FcC^+H_2 (Fc = ferrocenyl) formation ($3.42 \text{ s}^{-1} \text{ M}^{-1}$) and for nucleophilic additions of water ($50.6 \text{ s}^{-1} \text{ M}^{-1}$) and pyridine ($3.77 \times 10^5 \text{ s}^{-1} \text{ M}^{-1}$) to the same carbocation were determined. Corresponding secondary α -hydrogen isotope effects on FcC^+H_2 formation (ca. 1.28) were found, and were calculated for additions of water (ca. 0.78) and pyridine (ca. 0.79) to FcC^+H_2 . These results were discussed in terms of some possible structural models of FcC^+H_2 .

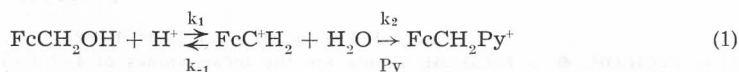
INTRODUCTION

Considerable evidence is available¹⁻⁵ regarding the stability and structure of ferrocenylalkyl carbocations. However, there are still uncertainties as to whether interaction of an α carbon (or β carbon^{2,3,10,13}) with electrons from the region between two cyclopentadienyl rings via the cyclopentadienyl ring system^{8,9,14} is mainly due to the unusual stability of the ferrocenylalkyl carbocations or some direct bonding between iron and the cationic center^{4,6,10-13} also contributes to this phenomenon. Accordingly, structural models involving conjugation with the π -system only^{8,9} (II), or metal participation^{6,7,11,12} (I) have been suggested. Within each of these two concepts there are also differences in the geometry of the several structural models suggested. The aim of this investigation was to obtain some additional insight into the above problem.



RESULTS

Rate parameters k_1 , k_{-1} , k_2 and corresponding secondary α -hydrogen kinetic isotope effects are reported here for the reaction system



(Fc = ferrocenyl, Py = pyridine). They were calculated from determined

TABLE I

Rate parameter ^a s ⁻¹ M ⁻¹	Compound		Secondary α -hydrogen kinetic isotope effect	
	FcCH ₂ OH	FcCD ₂ OH	k_1^H/k_1^D	
k_1	3.42 ± 0.18	2.68 ± 0.12	k_1^H/k_1^D	1.276
k_{-1}^b	50.58		k_{-1}^H/k_{-1}^D	0.784 ^c
k_2	3.77 × 10 ⁶		k_2^H/k_2^D	0.788 ^d

^a at 25 °C in water, with 0.8% v/v added acetonitrile and an ionic strength of 0.5 maintained by benzyltrimethylammonium chloride.

^b Calculated using k_1 and pK_R value of FcC⁺H₂ from ref. 16.

^c On the assumption of microscopic reversibility taking $k_{-1}^H/k_{-1}^D = k_1^D/k_1^H$. Such an approach seems to be reasonable since similar results have been obtained experimentally (see ref. 1).

^d The ratio of the slopes is 1.2804.

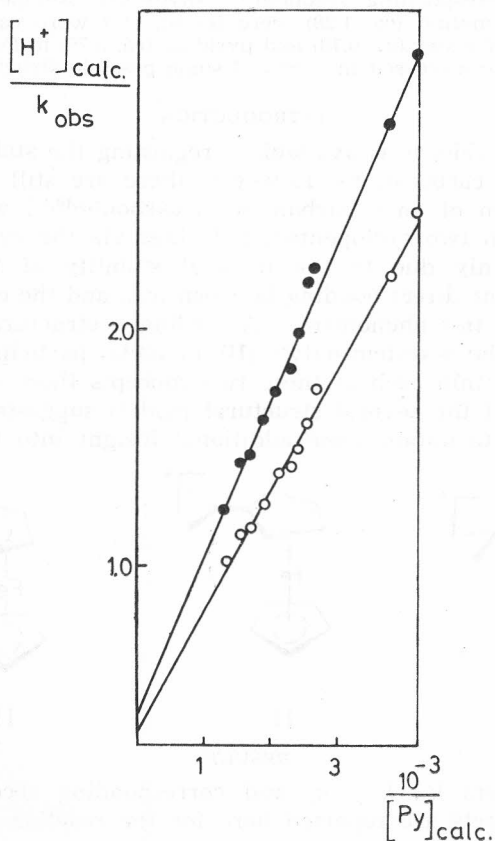


Figure 1. Plot of $[H^+]_{calc}/k_{obs}$ vs. $1/[Py]_{calc}$

○ — FcCH₂OH. ● — FcCD₂OH. Points are the mean values of 4–6 individual rate constants. Plots were computed using a multiple linear regression analysis on a PDP — 11 computer system.

first-order rate constants for addition of ferrocenylmethyl carbinol into water pyridinium hydrochloride solution, and from the reported pK_R value¹⁶ for the ferrocenylmethyl carbocation (FcC^+H_2). The intermediate of FcC^+H_2 and steady-state approximation conditions for the reacting system (1) were assumed, where

$$\frac{1}{k_{obs}} = \frac{k_{-1} [H_2O]}{k_1 k_2 [Py] [H^+]} + \frac{1}{k_1 [H^+]} \quad (2)$$

A linear relationship (with correlation coefficient of 0.979) between

$$\frac{[H^+]_{calc}}{k_{obs}} \quad \text{and} \quad \frac{1}{[Py]_{calc}}$$

was obtained over a tenfold range of pyridinium hydrochloride concentrations (Figure 1). Results are summarized in Table I.

EXPERIMENTAL

Preparations. Ferrocenylmethyl carbinol and ferrocenyl-1, 1-dideuteriomethyl carbinol were prepared in accordance with the procedure described in ref. 15. Pyridinium hydrochloride was prepared from pyridine and dry HCl and recrystallized three times from ethanol/ether.

Kinetics. Ferrocenylmethyl carbinol in acetonitrile was added into water pyridinium hydrochloride solution of appropriate concentration. The $FcCH_2Py^+$ formation rate was followed spectrophotometrically (using an Cary 16 K spectrophotometer) at 405 nm. Good first-order kinetics are obtained for at least four half-lives. Individual rate constants were computed using a nonlinear regression analysis on a PDP 11 computer system.

Ionic strength was maintained at 0.5 with benzyltrimethylammonium chloride. All measurements were carried out at 25 °C in a carefully thermostatted cell holder. $[H^+]$ was calculated from pK_a value (5.248 ± 0.004 under conditions reported here) of pyridinium hydrochloride, obtained from titration data.

DISCUSSION

As expected, the rates of formation and nucleophilic addition of water to the ferrocenylmethyl carbocation are rather different from those of more stable and to some degree sterically hindered secondary and tertiary carbocations^{18,19}. The k_{-1} value should be regarded with caution, since it is calculated using k_1 determined from data for reactions in media of low acidity, and the pK_R of FcC^+H_2 is measured (ref. 16) in media of very strong acidity (aqueous H_2SO_4). It is well known however that k_1 and k_{-1} values are sensitive to medium effects. This problem has been discussed by Bunton¹⁶ et al. Nevertheless, the k_{-1} value reported Bunton¹⁶ ($55 \text{ s}^{-1} \text{ M}^{-1}$) is not very different from the k_{-1} value (ca. $50.6 \text{ s}^{-1} \text{ M}^{-1}$) referred to in this work. Rate constant for addition of pyridine to FcC^+H_2 may be compared with that for addition of water to the same cation ($k_{-1} = 55 \text{ s}^{-1} \text{ M}^{-1}$, ref. 16).

Although general base catalysis was observed²⁰ in reactions of triarylmethyl carbocations with water, it seems (see Figure 1) that general acid-base catalysis in reaction (1) is not important under the conditions reported here²¹.

The secondary α -hydrogen kinetic isotope effect (ca. 1.28) upon the formation of the ferrocenylmethyl carbocation from ferrocenylmethyl carbinol

suggested²² that there is a $sp^3 \rightarrow sp^2$ hybridisation change at the reaction centre in the transition state*.

However, the fact that the magnitude of this effect (roughly 14% per one deuterium atom) differs from a maximum isotope effect for an oxygen leaving group (about 22% per deuterium)²³, may be interpreted in several ways. Bunton and Watts¹ obtained similar results for the formation, and the corresponding isotope effect for solvolysis of Fc_2C^+H and $p\text{-MeOC}_6\text{H}_4C^+HFc$ in aqueous acidic media and they suggest that there is appreciable $C \dots O$ bond formation in the transition state for carbocation solvolysis. On the other hand, the iron hyperconjugation formulation proposed by Traylor⁸ and depicted as a resonance hybrid of the canonical structure (II) and (III) may also explain the observed isotope effect.

Finally, if there is some direct iron participation in the stabilisation of the cationic centre along with some double bond character of the exocyclic bond, an isotope effect smaller than the maximum expected should result. Recent crystal X-ray analysis⁴ of ferrocenyldiphenyl carbocation probably support such an explanation. It seems, however, that there is no reasonable way to decide between several interpretations.

The calculated secondary α -hydrogen kinetic isotope effect for addition of pyridine to ferrocenylmethyl carbocation (about 14% per deuterium) is the same as that for addition of water to the same carbocation. Probably that is not surprising, because comparison between maximum secondary deuterium isotope effects for an oxygen²³ leaving group and leaving fluoride^{24,25}, and calculated isotope effect for a carbon-carbon bond breaking²⁶ with calculated H/D fractionation factors from valence force fields, relative to acetylene, shows that isotope effect are similar in magnitude for carbon, fluorine and nitrogen leaving atoms^{27,15}. In addition, Cordes²⁸ et al. pointed out that the equilibrium isotope effects for addition of nitrogen and oxygen nucleophiles to esters should be about the same.

The question of why the secondary α -hydrogen kinetic isotope effect for a nitrogen leaving group¹⁵ and for the addition of nitrogen nucleophiles¹ to ferrocenylalkyl carbocations differs from the present result remains a subject for further investigation in this laboratory.

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* Some criticism may be made in connection with (see also ref. 21) $FcCH_2OH + H^+ \rightleftharpoons FcCH_2OH_2^+$ pre-equilibrium. However, if this is the case, the resulting inductive isotope effect of two deuterium may be only small fraction of the isotope effect observed. Thus, for example, in quaternization reactions of *N,N*-dimethylaniline and *N,N*-dimethyl- d_6 -aniline with methyl toluenesulfonate the kinetic isotope effect was found to be $k_D/k_H = 1.133$ (see ref. 22, p. 264). Furthermore, the inductive isotope effect resulting from the latter pre-equilibrium should also be inverse, while a normal kinetic isotope effect for FcC^+H_2 formation was observed.

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SAŽETAK**Ferocenilalkil karbokationi. Brzine stvaranja i nukleofilnih adicija ferocenilmetil karbokationa***S. Uršić*

Određene su konstante brzine stvaranja FcC^+H_2 (Fc = ferocenil), ($3.42 \text{ s}^{-1} \text{ M}^{-1}$) i nukleofilne adicije vode ($50.6 \text{ s}^{-1} \text{ M}^{-1}$) i piridina ($3.77 \times 10^6 \text{ s}^{-1} \text{ M}^{-1}$) na taj kation.

Određen je sekundarni α -deuterijski izotopni efekt (oko 1.28) za stvaranje FcC^+H_2 . Izračunan je odgovarajući efekt za adiciju vode (oko 0.78) i piridina (oko 0.79). Ovi rezultati diskutirani su u odnosu na neke moguće strukturne modele FcC^+H_2 .

FARMACEUTSKO-BIOKEMIJSKI FAKULTET

ZAVOD ZA KEMIJU

SVEUČILIŠTA U ZAGREBU

41000 ZAGREB

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