Tetrahedron Letters No. 13, 1-8, 1960. Pergamon Press Ltd. Printed in Great Britain.

THE ROLE OF IRON IN CARBONIUM ION REACTIONS OF FERROCENE DERIVATIVES

D. S. Trifan and R. Bacskai
Plastics Laboratory, Princeton University
Princeton, N. J.

(Received 6 May 1960)

Recently, some useful quantitative rate comparisons between certain metallocenyl and triphenyl systems were provided by Richards and Hill[1] for solvolysis reactions proceeding via α-metallocenyl carbonium ions which showed the solvolysis rates in 80% acetone-water mixture at 30° for metallocenyl carbinyl acetates to be on the same high order of magnitude as triphenylcarbinyl acetate. Included in their series was the heteroannular acetate, α-acetoxy-1,1'-trimethyleneferrocene which was observed by these authors to proceed more slowly than the analogous open chain compound,

---

[1] J. H. Richards and E. A. Hill, J. Amer. Chem. Soc., 81, 3484 (1959).

[2] Calculated from data of Richards and Hill[1], although the value 132 is used in their text.

methylferrocenylcarbinyl acetate, by a factor of 29 [2], a rate depression which they attributed to the structurally enforced non-planarity of the resulting carbonium ion. But to account for the fact that this heteroannular compound nevertheless still underwent solvolysis via a carbonium ion mechanism, they suggested for this special case the possibility that stabilization of the non-planar ion might be obtained by participation of the iron electrons.

Work on a comprehensive series of ferrocenyl alcohols has been in progress in this laboratory for an extended period of time, studying and defining the active and general role of the iron atom and its electrons acting as proton acceptors in intramolecular hydrogen bonding reactions[3]. Especially since the suggestion of Richards and Hill had been limitedly made only to account for the special case of the enforced non-planar ion, and the overall high solvolytic reactivities were considered to be in consistent accord with M.O. treatment for metallocenyl systems[4], it was therefore of interest to us to apply experimental tests to ascertain that metal electron participation might here too be a completely general

---

[3] D. S. Trifan and R. Bacskai, unpublished results.

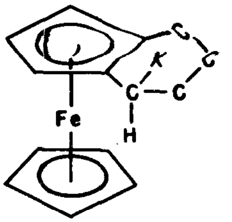
[4] J. H. Richards, Abstracts 135th Meeting of American Chemical Society, April 5-10, 1959, Boston, Mass., p. 86-O.

phenomenon for the chemical reactions of all suitably constituted metallocene compounds proceeding via α-cationic intermediates.

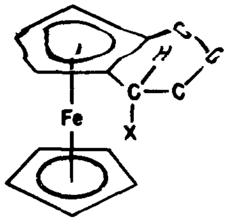
In this preliminary report we wish to present briefly some results on the role of the metal atom with respect to rates and stereochemistry which appear to be of fundamental importance and generality for all metallocene reactions of this type.

General Metal Participation

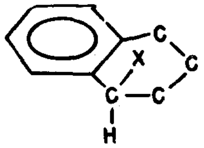
Two ferrocene derivatives of great utility in studying the role of the iron atom in this and related respects are the two isomeric α-substituted 1,2-tetramethyleneferrocenes, represented by structures I and II and designated _exo_- and _endo_-, respectively.



I



II



III

From the corresponding ketone[5], the isomeric alcohols, I and II (X = OH), were prepared by $LiAlH_4$ reduction. Separation of the two alcohols (11% exo-, m.p. 71.5-72.5°; 89% endo-, oil) and ready assignment of the correct corresponding structure by at least four unequivocal and independent criteria provided the necessary materials for the preparation of the exo- and endo-acetates, I and II ($X = OCOCH_3$), m.p. 64-65° and 49-50°, respectively, for comparative solvolysis rate measurements. The analogous phenyl ester, α-tetralyl acetate, III ($X = OCOCH_3$), b.p. 156°/25 mm., was also included for comparative rate purposes.

The data summarized in Table 1 show a large rate gap between the exo- and endo-isomers resulting from the difference in relative geometry between the iron atom and the departing substituent and permit the important conclusion that in the exo- case (I) where the iron atom is located backside to the acetoxy group, the iron electrons are participating in a backside displacement of the anion in the rate determining ionization process. Where backside geometry between the iron and acetoxy group cannot be attained, as in

---

[5] K. L. Rinehart, Jr. and R. J. Curby, Jr., *J. Amer. Chem. Soc.*, **79**, 3290 (1957).

TABLE 1. Solvolysis rates[a] in 80% acetone-water at 30°.

COMPOUND	k, sec^{-1}	Rel. rate
exo-α-Acetoxy-1,2-tetramethylene-ferrocene (I, X = $OCOCH_3$)	7.43×10^{-4}	2240
endo-α-Acetoxy-1,2-tetramethylene-ferrocene (II, X = $OCOCH_3$)	3.31×10^{-7} [b]	1
α-Tetralyl acetate (III, X = $OCOCH_3$)	5.50×10^{-10} [b]	0.00166
Methylferrocenylcarbinyl acetate (IV)	1.84×10^{-4}	556

[a] Clean first order kinetics were observed in all cases. Reactions were followed to 80-90% for the ferrocene derivatives.

[b] Extrapolated from data at higher temperatures.

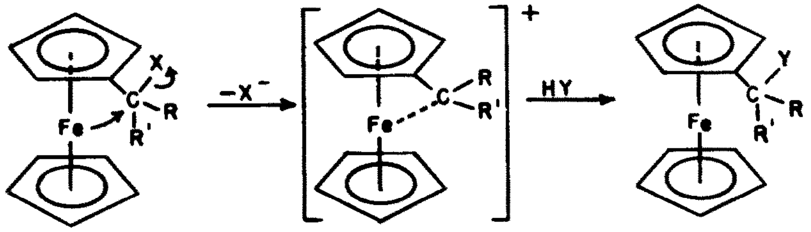
the constrained _endo_- structure (II), no such iron participation is possible and a sharp 2240-fold drop in rate is observed. This rate factor is significant in terms of evidence of iron electron participation in the rate step since it is entirely reflected in the enthalpy of activation, $\Delta H^{\ddagger}$. Also, since side chains are usually not rotationally constrained as in the test structures I and II, and suitable backside geometry between the iron atom and substituent group is readily attainable, it is clear from the comparable high order of solvolysis rates for such ferrocene derivatives in general, e.g. ferrocenylmethylcarbinyl (IV), etc.[1], that iron electron participation must be occurring as a characteristic and general phenomenon in reactions proceeding through α-ferrocenyl cationic intermediates. Analogously, the same metal electron participation must be occurring for reactions involving other metallocenyl cations, judging from the even greater solvolysis rates of the osmocenyl and ruthenocenyl examples[1].

The rate contrast between the endo-isomer, II ($X = OCOCH_3$) and α-tetralyl acetate, III ($X = OCOCH_3$), would appear at first to suggest that some residual electronic driving force is still present in the endo-isomer compared to its phenyl analog. However, this is not the case as shown by the fact that the $\Delta H^{\ddagger}$ of activation of the two compounds are actually in the reverse sequence. The rate difference here is due instead to a much smaller negative entropy of activation, $\Delta S^{\ddagger}$, for the ferrocenyl compared to the phenyl compound, an observation which applies generally for all of the ferrocenyl-phenyl pa~~rr~~s we have measured to date.

Cation Structure and Stereochemistry

A second important finding which has resulted from this study concerns the structure and stereochemistry of α-ferrocenyl carbonium ions.

Evidence for the metallocarbocation structure, VI,



V VI VII

involving covalent bonding between the iron atom and the carbonium carbon comes from the absolute stereochemical purity of the exo-alcohol I (X = OH) which is the sole alcohol product found in the 80% acetone-water solvolyses of both _exo_- and _endo_-esters. With the precision available from our chromatographic and infrared spectroscopic methods, it was possible to establish that I (X = $OCOCH_3$) and II (X = $OSO_2C_6H_4CH_3$) both proceeded to I (X = OH) with a purity of not less than 99.6 and 99.94%, respectively. This highly stereospecific result may be compared with the 89:11 _endo_-: _exo_-alcohol ratio from the $LiAlH_4$ reduction of the ketone which provides an approximate (but reversed) indication of the ratio of _exo_-: _endo_-solvent attack which might have been expected if final solvolysis product had been produced via a non-bonded classical-type ion.

While the anchimerically unassisted solvolysis of II must first have proceeded through a planar classical-type ion which quickly transformed into the stabler metallocarbonium ion structure (VI) before any reaction with solvent could proceed, solvolysis of I where metal electron participation occurs can lead directly to the metallocarbonium ion. Thus, in the general case of open-chain derivitives, V ⟶ VI ⟶ VII, one would therefore expect reaction to proceed with overall retention of configuration as a consequence of metal electron participation and cation structure.

A final pertinent topic of interest here is the question of possible iron participation and cation structure for β-metallocenyl derivatives. Results to date show a solvolysis rate factor in 80% acetone-water of 537 for β-ferrocenylethyl vs. β-phenylethyl p-toluenesulfonates, of which only a factor of ca. 3 is reflected in the ΔH^{*} terms, however.

The extent to which iron participation may still be influencing rate and stereochemistry remains under study through appropriate rate and stereochemical experiments. These results and a fuller presentation of the above data will be published subsequently.