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RESONANCE STABILIZATION OF α-FERROCENYL CARBONIUM IONS

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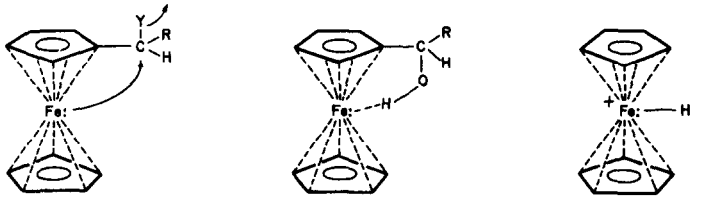
The rapid rate and stereospecificity of solvolyses of α-ferrocenyl acetates (1) and α-ferrocenylethyl chloride (2), internal hydrogen bonding in α-ferrocenyl-carbinols (3), and the n.m.r. spectrum of protonated ferrocene (4) have all been attributed to nucleophilic or basic participation of the non-bonding electrons on the metal atom as shown below.

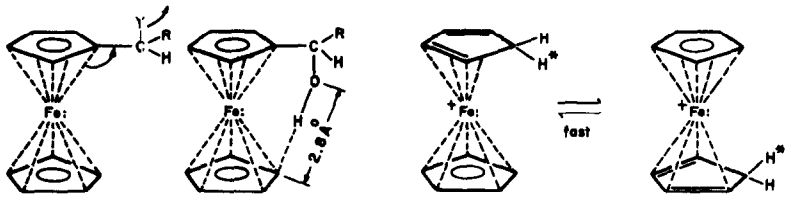
Postulated Metal Participation in Ferrocene Reactions



Solvolysis H-Bonding Protonation

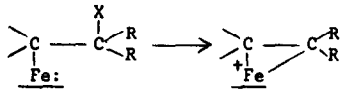
The following alternative formulations are also consistent with the recorded evidence.

Postulated Carbon Participation in Ferrocene Reactions

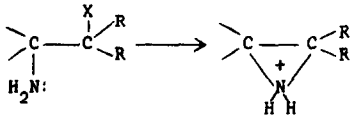


Solvolysis* **H-Bonding** **Protonation****

In the case of solvolyses of α-ferrocenylethyl derivatives the reported rate increases of about 10^{13} over the ethyl derivatives are inordinately large for "direct backside metal participation" (1b) (Equation 1) when compared to an increase of about 10^{5} for participation of the β-amino group (5a) (Equation 2).



(1)



(2)

The large rate enhancement is comparable to the effect of an

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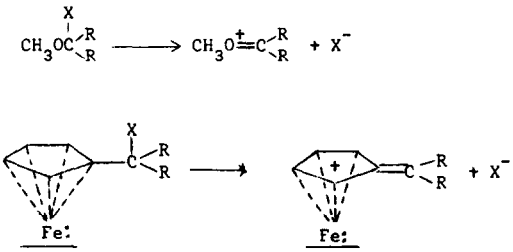
* This carbon participation in solvolysis is most closely analogous to E_2 elimination, which occurs in other β-metalloalkyl halides and derives its driving force from double bond (fulvene) formation rather than iron participation.

** It has been pointed out that ferrocene protodesilylation results could be explained on the basis of direct formation of an exocyclic proton σ-complex without metal participation, R. A. Benkeser, Y. Nagai, and J. Hooz, J. Am. Chem. Soc., 86, 3742 (1964). These considerations and the implied ring-to-ring migrations also apply to other electrophilic reactions.

α-methoxy group on similar solvolyses (6) and this kind of resonance effect seemed more attractive to us. (See equations 3 and 4.)



(3)

(4)

The σ^{+}_{para} values of substituents such as methoxy or hydroxy are generally employed as measures of the ability of the group to stabilize transition states or intermediates which delocalize electrons from these groups, i.e., their resonance effects (7). The σ^{+}_{para} of the ferrocenyl group should likewise reflect its resonance effect and a comparison of σ^{+}_{para} for methoxy and ferrocenyl groups will reveal their relative resonance stabilizing abilities.

If we assume that the methoxy group stabilizes carbonium ions only by resonance in either the alpha or the para positions (8), then we may write (5b)

$$\log\left(\frac{k_{\alpha\text{-MeO}}}{k_{\alpha\text{-H}}}\right) \propto \log\left(\frac{k_{p\text{-MeOC}_6H_4}}{k_{\phi}}\right) = \rho\sigma^{+}_{p\text{-MeO}} \qquad (5)$$

Then, for the ferrocenyl group,

$$\log\left(\frac{k_{\alpha\text{-fer}}}{k_{\alpha\text{-H}}}\right) = \rho\sigma^{+}_{p\text{-fer}} + L^{*}_{fer} \qquad (6)$$

* See reference (5c).

where $\rho\sigma^{+}_{p\text{-fer}}$ represents the resonance stabilization of the ferrocenyl group and L_{fer} is the anchimeric assistance provided by the non-bonding electrons on iron. Subtracting 5 from 6 and rearranging terms leads to

$$L_{fer} = \log\left(\frac{k_{\alpha\text{-fer}}}{k_{\alpha\text{-MeO}}}\right) + \rho\left(\sigma^{+}_{p\text{-MeO}} - \sigma^{+}_{p\text{-fer}}\right) \qquad (7)$$

We have determined $\sigma^{+}_{p\text{-fer}}$ to be -0.71 and $\sigma^{+}_{m\text{-fer}}$ to be -0.0 in two ways from the data of Table I and Figure 1.

TABLE I

Relative Rates of Solvolyses of Chlorides at 25°

X	$XCHClCH_3$ [b,e]	$XC_6H_4CHClCH_3$ [c]	$XC_6H_4CCl(CH_3)_2$ [d]
H	$\sim 10^{-13}$	(1)	(1)
Fer [a]	(1)		
MeO	>2		
o-MeO			105
m-MeO			0.61
p-MeO		53,000	3360
o-Fer [a]		84	
m-Fer		0.8	
p-Fer		20,000	

a - Fer = ferrocenyl; b - Ether - ethanol solvent;
c - Some values extrapolated from other temperatures.
Solvent, 95% ethanol - 5% water by volume;
d - Reference 7; e - Hill[2] reported that α-ferrocenylethyl chloride solvolyses 500 times faster than trityl chloride and Ballinger et. al.[6] reported that α-methoxyethyl chloride solvolyses at least 1000 times faster than trityl chloride.

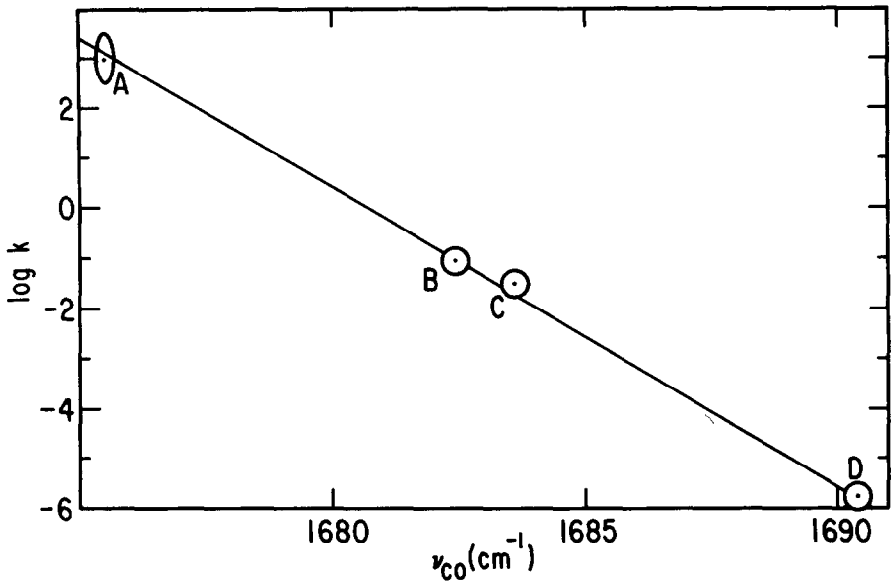


Figure 1. A plot of log k for solvolysis in aqueous 95% (volume) ethanol of $RCHClCH_3$ against the carbonyl stretching frequency in carbon tetrachloride of $RCOCH_3$. A- R = ferrocenyl, B- R = p - methoxyphenyl, C- R = p-ferrocenylphenyl, D- R = phenyl. The rate for A was estimated from the rates and activation enthalpy of reference 2 and the solvent dependence of similar solvolyses given in reference 6. The estimated rate should certainly be accurate within a factor of ten. The stretching frequencies were measured in carbon tetrachloride on a Cary 90 Infrared Spectrophotometer.

These values are very close to $\sigma^{+}_{p\text{-MeO}} = -0.78$ and $\sigma^{+}_{m\text{-MeO}} = +0.047$ determined by Brown et. al. (7).

The value of ρ is estimated from $\log \frac{k_{\alpha\text{-MeO}}}{k_{\alpha\text{-H}}} / -0.78$ to be about -16 and $\frac{k_{\alpha\text{-fer}}}{k_{\alpha\text{-MeO}}} \leq \frac{1}{2}$ (Table I). Therefore, $L_{fer} \leq \log \frac{1}{2} -16(-0.07) \leq 0.8$. This means that anchimeric assistance by iron contributes at most a factor of six and the remaining factor of about 10^{12} is apparently due to delocalization (i.e. double bond formation) (9).

We have reached the same conclusion by another experimental correlation. Figure 1 shows a plot of log k for solvolyses of $RCHClCH_3$ against the carbonyl stretching frequencies of $RCOCH_3$.

Both Foote (11) and Schleyer (12) have indicated that such a correlation does not obtain when anchimeric assistance occurs. Because the α-ferrocenylethyl chloride correlates effectively with the stretching frequency of the corresponding ketone we again conclude that direct participation by iron does not increase the rate of solvolysis appreciably.

A third, although less conclusive, indication that anchimeric assistance is not important in these systems is seen by comparing ortho, meta, and para methoxy with ferrocenyl groups. The similarity in the effect of these two groups is striking. The ortho ferrocenyl group can be brought into a very good position for backside participation by a slight twist. Yet this group is relatively less effective in the ortho position than is the methoxy group. Even the meta ferrocenyl group is not so far from the ortho or para positions (3.6Å) to prevent some d-orbital overlap with these positions. However, m-ferrocenyl-α-phenethyl chloride solvolyses even more slowly than its inductive effect predicts.

On the basis of these experiments we conclude that the ferrocenyl group is best considered as a somewhat complexed cyclopentadienide anion in which its ability to supply electrons by resonance is severly decreased

by this complexing. Nevertheless, the remaining resonance effect on solvolysis rates is about 6 kcal./mole larger than that of a phenyl group.

Although the iron atom could bond to the α-carbon after the rate-limiting step to govern stereochemistry, the stereospecificity of these reactions can be explained on the basis of steric effects.

The isomeric α-ferrocenylphenylethyl chlorides were solvolyzed in 95% aqueous ethyl alcohol, in which the pseudo first-order reactions were followed conductimetrically. The products from p-ferrocenyl-α-phenylethyl chloride solvolysis consist of over 80% of the anticipated ethyl ether and carbinol in a ratio of 5.8:1.

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8. The use of σ^{+}_{para} values to correlate resonance stabilizations in the α-position will be discussed later.

9. We are assuming, with some justification[7, 10] that anchimeric assistance by an S_N2' attack at the para position in a benzyl chloride solvolysis is negligible. However, this matter is under investigation.

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