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Acetolysis of Ferrocenylmethyl Benzoate. High Secondary α-Deuterium Kinetic Isotope Effect for Primary Carbon–Oxygen Cleavage*

SMILJKO AŠPERGER**, DUŠANKA PAVLOVIĆ

Department of Chemistry, Faculty of Pharmacy and Biochemistry, University of Zagreb, Zagreb, Croatia (Yugoslavia)

ZORAN KUKRIĆ and DUŠAN ŠUTIĆ

Department of Chemistry, Faculty of Natural Sciences and Mathematics, University of Sarajevo, Sarajevo, Bosnia and Hercegovina (Yugoslavia)

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Abstract

Secondary α-deuterium kinetic isotope effect (*KIE*) in acetolysis of ferrocenyl-1,1-dideuteriomethyl benzoate was determined at 298 K as $kH/kD = 1.50$ (22.5% per D). This appears to be one of the largest *KIE* observed for carbon–oxygen cleavage. The solvolysis exhibits a 'special salt effect', and a common ion rate depression effect, indicating the presence of solvent-separated ion pairs and the return to tight pairs. The high value of *KIE* in acetolysis strongly suggests that the acetolysis is a limiting dissociative process with the carbonium ion transition state, stabilized mainly by conjugation with the π-system. The entropy of activation (-30 J K^{-1} mol^{-1}) is very similar to those values we previously determined in ethanolyses of ferrocenylmethyl acetate and benzoate (-22 and -25 J K^{-1} mol^{-1}), where the *KIE* was only 11.4% per D. In the latter reactions the stabilization of the transition state probably involves some Fe–C_{exo} bond formation. It appears that the mode of stabilization of the ferrocenylmethyl cation depends on the type of solvolysis and on the nature of the media: high *KIE* is observed in solvents of high ionizing power. Entropies of activation cannot help in distinguishing between the two possible modes of stabilization.

Introduction

The α-metallocenyl carbonium ions are very stable due to the electron releasing effect of the metallocenyl group [1]. This enabled isolation of their stable salts [2]. The nature of the ferrocenylmethyl cation ($FcCH_2^+$) has been extensively studied [3, 4]. The dilemma is whether the great stability of the $FcCH_2^+$ is due to a direct participation of iron electrons (Fe–C_{exo} bond formation) or to conjugation with the π-system of the pentadienyl rings, when electrons from iron–carbon bonds are involved in stabilization through the ring bearing methylene group. There is also a possibility that both modes of stabilization can occur, depending on the type of solvolysis and on the nature of the media. This belief is based on our results of α-D kinetic isotope effects (*KIE*) in acetolysis of ferrocenyl-1,1-dideuteriomethyl benzoate, in which a very large α-D effect for primary carbon–oxygen cleavage of 50% per D_2 (22.5% per one D (geometric mean)) is observed. This result is confronted with our earlier results of a very small α-D effect (about 3% per D) in hydrolysis of ferrocenyl-1,1-dideuteriomethyltrimethylammonium ion [4a] and a *KIE* of about 11.4% per D in ethanolyses of ferrocenyl-1,1-dideuteriomethyl acetate and benzoate, respectively [4b].

After the first observation of sizable α-deuterium effects in presumed carbonium ion processes reported independently by four different groups [5], these effects were used to decide if the mechanism was a dissociative or a synchronous displacement. The very large α-D effect we found in acetolysis of $FcCD_2O_2CPh$ ($kH/kD = 1.50$) indicates that there is no direct iron electron participation in the reaction transition state. On the other hand a reduced *KIE* from its maximum suggests a certain participation, e.g. neighboring, entering and/or leaving groups, or metal participation. As we pointed out earlier [4b] the maximum *KIE* is observed when the rate-determining step involves intimate and solvent-separated ion pairs transformation [6]. The solvolyses we investigated seem to meet those requirements. They are limiting type solvolyses, they exhibit a 'special salt effect' and a common ion rate depression effect [7].

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**Author to whom correspondence should be addressed.

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TABLE 1. Rates of acetolyses of 5 × 10^{-4} mol dm^{-3} $FcCH_2O_2CPh$ in glacial acetic acid

T (K)	$10^4 \times k^{H}_{obs}$ (s^{-1})	$10^4 \times k^{H}_{obs}$ (s^{-1}) (mean)
293.14	3.49	3.41 ± 0.03[a]
	3.37	
	3,43	
	3.36	
298.14	6.33	6.25 ± 0.08[a]
	5.99	
	6.47	
	6.20	
	5.98	
	6.48	
	6.23	
	6.33	
304.64	13.10	13.33 ± 0.23[a]
	13.80	
	13.09	
308.14	18.00	17.85
	17.70	

[a] Standard error of the mean.

TABLE 2. Rates of acetolyses of 5 × 10^{-4} mol dm^{-3} $FcCD_2O_2CPh$ in glacial acetic acid

T (K)	$10^4 \times k^{D}_{obs}$ (s^{-1})	$10^4 \times k^{D}_{obs}$ (s^{-1}) (mean)
298.14	4.22	4.16 ± 0.03[a]
	4.19	
	4.04	
	4.21	
	4.12	
	4.20	

[a] Standard error of the mean.

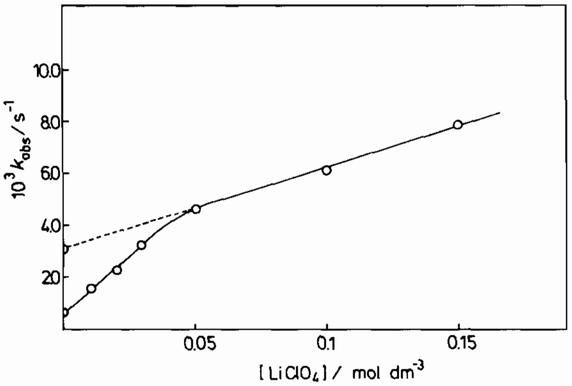


Fig. 1. Salt effect of lithium perchlorate on solvolysis of 5 × 10^{-4} mol dm^{-3} ferrocenylmethyl benzoate in glacial acetic acid at 298 K.

Results

Kinetic data of the rates of acetolysis of ferrocenylmethyl benzoate and ferrocenyl-1,1-dideuteriomethyl benzoate in glacial acetic acid are given in Tables 1 and 2. The activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were determined from the plots $\log(k^{H}_{obs}/T)$ versus $1/T$, which were good straight lines. The values found were 82.3 ± 2.6 kJ mol^{-1} and −29.9 ± 5 J mol^{-1} K^{-1}, for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, respectively. At 298.14 K the α-D *KIE* $kH/kD = 6.25/4.16 = 1.50$, or 22.5% per one deuterium atom (geometric mean).

Salt Effects in Acetolysis of Ferrocenylmethyl Benzoate

Common ion rate depression effect

The addition of sodium benzoate (0.1 mol dm^{-3}) to a solution of 5 × 10^{-4} mol dm^{-3} $FcCH_2O_2CPh$ in glacial acetic acid reduced the reaction rate by about 25%. A calculation similar to that used by Swain *et al.* [8] for the common ion rate depression effect in trityl chloride solvolysis shows that the ferrocenylmethylcarbonium ion reacts with acetate 4.0 times as fast as with benzoate. This is to be expected because acetate is a better nucleophile than benzoate.

Special salt effect

Figure 1 reveals a combination of special [7a, 9] and normal [10] salt effects, very similar in magnitude to those previously noted in acetolysis of 2-*p*-annisyl *p*-toluenesulfonate [7a]. Perchlorate converts some of the solvent-separated ion pairs to solvent-separated perchlorate ion pairs. The initial ionization of the ferrocenylmethyl benzoate yields a 'tight' (intimate) ion pair which then converts to a solvent-separated ion pair. Solvent-separated ion pairs may revert to 'tight' ion pairs or give products, as shown by the following scheme

$$\mathrm{FcCH_2O_2CPh} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{FcCH_2{}^{+}O_2CPh^{-}} \underset{k_{-2}}{\overset{k_2(\mathrm{HAc})}{\rightleftharpoons}}$$

$$\begin{tikzcd} \mathrm{FcCH_2{}^{+}\|O_2CPh^{-}} \arrow[rr, shift left, "k_3"] \arrow[dr, "k_4"'] & & \mathrm{FcCH_2{}^{+} + O_2CPh^{-}} \arrow[ll, shift left, "k_{-3}"] \arrow[dl, "k_5"] \\ & \mathrm{FcCH_2O_2CCH_3} & \end{tikzcd} \qquad (1)$$

From Fig. 1 it can be seen that, at perchlorate concentrations larger than 0.05 mol dm^{-3}, the external return of a solvent-separated to 'tight' ion pair is practically prevented. According to eqn. (1) the sole reaction product is $FcCH_2O_2CCH_3$. However, this is true only if the acetolysis is carried out in the absence of oxygen. If oxygen is present iron(II) is partly oxidized to iron(III), so that ferricynium salts are formed [11]. Therefore we carried out acetolyses under oxygen-free argon (see 'Experimental').

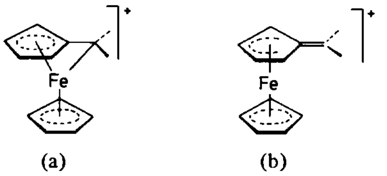
Discussion

Previously we reported [4a] that the α-deuterium *KIE* (kH/kD) in the hydrolysis of (ferrocenyl-1,1-dideuteriomethyl)trimethylammonium iodide was about 3% per D, and in ethanolyses of ferrocenyl-1,1-dideuteriomethyl-acetate and benzoate [4b] kH/kD = 1.24 (geometric mean = 11.4% per D). In general, the maximum *KIE* observed depends appreciably on the nature of the leaving group. On the other hand it has been estimated that maximum α-D *KIE* for nitrogen and oxygen leaving groups have similar magnitudes [4a]. Therefore the very low value of the α-D effect for the $N(CH_3)_3$ leaving group is puzzling. A possible explanation might be that a direct displacement reaction competes with hydrolysis. This might well be, since the reaction center is primary and water is relatively nucleophilic, while the leaving group is uncharged.

The maximum α-D *KIE* for an oxygen leaving group was found to be 22% [12, 13] and 23% by other investigators [6a]. For the carbon–nitrogen bond rupture the maximum *KIE* has not been measured. The primary alkyl derivatives normally do not solvolyse by the limiting dissociative mechanism, hence the maximum *KIE* for the primary derivatives is not known, but calculations [6] and experiments [14] suggest that the magnitude of *KIE* might be larger with the primary derivatives than with secondary ones [4b]. The kinetic and stereochemical evidence led to the conclusion that the solvolyses of β-ferrocenylalkyl tosylates are dissociative in nature and very nearly 'limiting' [3b, 15]. The rates of solvolyses in various media can be summarized as suggested by Winstein *et al.* [16] in terms of the ionizing power and nucleophilicity of the solvent. In a limiting solvolysis the rate depends on the ionizing power and not on the nucleophilicity of the solvent. Thus the rates of limiting solvolysis are about the same in solvents of comparable ionizing power but different nucleophilicity. On the other hand, such reactions which proceed by attack of solvent at carbon, with nearly synchronous displacement of a leaving group, proceed faster in solvents of greater nucleophilicity. These criteria led to the conclusion that acetolysis of β-ferrocenylalkyl tosylates are dissociative, nearly 'limiting' processes [3b]. As already pointed out for reactions limiting in character a kinetic α-D isotope effect is expected, which is near to the maximum [17]. In analogy with β-ferrocenylalkyl tosylates, the acetolysis of ferrocenylmethyl benzoate is expected to be an S_N1 (lim) process, and if there is no direct iron participation, the α-D *KIE* should be at its maximum, which is at least as large as that observed for limiting carbon–oxygen cleavage of secondary derivatives (22–23% per D). Indeed, in acetolysis of ferrocenylmethyl benzoate, we observed an isotope effect kH/kD = 1.50, one of the largest isotope effects observed for a carbon–oxygen cleavage in a solvolytic reaction. Such a high *KIE* strongly suggests that there is no significant solvent or leaving group participation in the transition state. In addition it should be concluded that there is also no significant direct participation of iron electrons in the transition state. Therefore, the structure of the transition state should involve predominantly conjugation with the π-system.

It is interesting to notice that the entropy of activation of the acetolysis is negative, about –30 J K^{-1} mol^{-1}. We obtained similar values in ethanolyses of ferrocenylmethyl acetate and benzoate (–22 and –25 J K^{-1} mol^{-1}, respectively); these reactions probably involve significant Fe–C_{exo} bond formation, as inferred from their α-D kinetic isotope effects of 11.4% per D (geometric mean) in both cases. These values are roughly one-half of the maximum α-D effect for carbon–oxygen cleavage.

Winstein and Heck [18] concluded on the basis of rate comparisons for solvolyses of a number of primary tosylates in ethanol, acetic acid and formic acid, that anchimerically unassisted solvolyses tend to have $\Delta S^{\ddagger}$ of about –75 J K^{-1} mol^{-1}, while assisted solvolyses have $\Delta S^{\ddagger}$ of about –30 J K^{-1} mol^{-1}. As already pointed out the stabilization of $FcCH_2^+$ can occur either through conjugation with the π-system, or by Fe–C_{exo} bond formation, as shown in Fig. 2. It appears that both modes of stabilization are associated with similar values of entropy of activation. Therefore no conclusion regarding the structure of the ferrocenylmethylcarbonium ion can be drawn from the entropy of activation data. In addition, the degree of solvation between the ground state and the zwitterionic transition state will be greater if the ground state is charged, like in hydrolysis of the (ferrocenylmethyl)-trimethylammonium ion where the entropy of activation is positive [4a] ($\Delta S^{\ddagger} = 54$ J K^{-1} mol^{-1}). A high α-D *KIE* of 21.6% per D (geometric mean) for carbon–nitrogen cleavage was recently observed in hydrolysis of the ferrocenylmethylquinolinium ion [19]. The same substrate, in the presence of 20% vol./vol. acetonitrile, gave an α-D *KIE* of only 11.2% per D.



(a) (b)

Fig. 2. Possible structures of ferrocenylmethylcarbenium ion (extreme cases): (a) involving Fe–C_{exo} bond formation; (b) conjugation with π-system. Formations of both structures exhibit very similar values of entropy of activation (about –30 J mol^{-1} K^{-1}).

The results presented, as well as our earlier data [4a, 4b], let us conclude that both modes of stabilization of ferrocenylmethylcarbonium ion occur in degrees which primarily depend on the ionizing power of the media.

The acetolysis of ferrocenylmethyl benzoate is about 15 times as fast as its ethanolysis [4b]. The steady state approximation, applied to the short lived intimate ion pair, $FcCH_2^+O_2CPh^-$, eqn. (1), shows that, if k_2 is neglected relative to k_{-1}, the α-D isotope effect is given by eqn. (2)

$$\frac{k^H}{k^D} = \frac{K_1{}^H k_2{}^H}{K_1{}^D k_2{}^D} \qquad (2)$$

This is especially so in the presence of $LiClO_4$, when there is no return from the solvent-separated ion pair.

Experimental

Preparations

All chemicals used, including deuterated compounds, were from Merck, analytical grade. Deuterated formaldehyde, needed for the preparation of bis(dimethylamino)dideuteriomethane [20], was supplied as a 30% vol./vol. solution of D_2CO (95%) in D_2O (99.8%) stabilized by CD_3OD.

Ferrocenylmethyl benzoate was prepared from the corresponding carbinol with benzoyl chloride in pyridine by the method previously published [21]; melting point 130–132 °C; $\bar{\nu}$(CO) 1745 cm^{-1}. *Anal.* Calc. for $C_{18}H_{16}O_2Fe$: C, 67.52, H, 5.04; Fe, 17.44. Found: C, 67.28; H, 5.20; Fe, 17.22%.

Ferrocenyl-1,1-dideuteriomethyl benzoate was prepared from deuterated carbinol in the same way. The ^1H NMR spectrum showed that deuteration of the methylene group is practically complete.

All preparations were carried out in oxygen-free argon atmosphere to avoid formation of ferricynium salts [11].

Kinetics

Acetolyses of ferrocenylmethyl benzoate as well as of their dideuterated analogues were carried out in glacial acetic acid. The kinetics were followed spectrophotometrically at 436 nm. Both benzoate and acetate contribute to the absorption at this wavelength, but the molar absorptivity of the former is nearly twice that of the latter (146.8 and 78 mol^{-1} dm^3 cm^{-1}, respectively). This difference was large enough for kinetic measurements in 10 cm cells. The thermostated absorption cell (25 ± 0.05 °C) was used as the reaction vessel. It was flashed several times with very pure argon (99.999% argon was further purified by passage through a cylindric glass column, inside diameter 7 cm, height 90 cm, filled with chromium(II) salts dispersed on silica*). The details of the apparatus for spectrophotometric measurements in oxygen free argon were described previously [22]. When the kinetics were followed in air at about 70% of completion the absorbance started to increase indicating formation of ferricynium salt.

Spectrophotometry

Cary 219 and Cary 16 K spectrophotometers were used for spectral measurements.

Apparatus

^1H NMR spectra were recorded on a JEOL 60 M Hz ^1H NMR spectrometer. IR spectra were measured on a Perkin-Elmer 783 IR spectrometer.

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