sulfate; 0.35 g, 4.1 mmol) and 2,2′-bipyridyl (1 mg) in THF (dry, 50 mL) under a nitrogen atmosphere at −60 °C. During the addition, the solution was allowed to warm to 5 °C. When the permanent pink end point was reached, the solution was recooled to −60 °C. A solution of the acid chloride of **3** (1.04 g, 2.06 mmol of **3**; prepared as usual in ether, thionyl chloride, and DMF and thoroughly dried in vacuo prior to use) in dry methylene chloride (15 mL) was then added dropwise over a period of 10 min. The mixture was stirred at −60 °C for 1 h, allowed to warm to 25 °C, and then poured into a flask containing diethyl ether (100 mL) and 1 N hydrochloric acid (30 mL). The resulting biphasic solution was stirred vigorously for 30 min. The organic layer was separated, washed with a saturated sodium bicarbonate solution (3 × 20 mL) and a saturated sodium chloride solution (3 × 20 mL), and then dried over magnesium sulfate. Filtration and evaporation of the filtrate afforded a residue which was purified by low-pressure chromatography (3 cm i.d. × 30 cm silica column; hexanes/ethyl acetate, 2:1 v/v; flow rate 12 mL/min). The desired fractions (indicated by UV monitoring) were collected and evaporated to a glass. Tritration with hexanes produced compound **12a** (0.45 g, 45%) as a solid which was crystallized from methanol.

Compound 12a: mp 141–141.5 °C; R_f 0.4 (solvent system d); $[\alpha]^{23}{}_D$ +89.3° (*c* 1.0, $CHCl_3$); IR (KBr) 2250 cm^{-1} (CN); ^{1}H NMR (360 MHz, $CDCl_3$) δ 2.94 (dd, H-4b, $J_{4b,4a}$ = 17 Hz, $J_{4b,1'}$ = 5.5 Hz), 3.14 (dd, H-4a, $J_{4a,4b}$ = 17 Hz, $J_{4a,1'}$ = 7.8 Hz), 3.51 (s, H-2), 4.53 (dd, H-4′, $J_{4',5'}$ = 13 Hz, $J_{4',3'}$ = 6.0 Hz), 4.64 (m, H-5′a,H5′b), 4.90 (ddd, H-1′, $J_{1',2'}$ = 4.6 Hz, $J_{1',4b}$ = 5.5 Hz, $J_{1',4a}$ = 7.8 Hz), 5.77 (dd, H-3′, $J_{3',2'}$ = 4.6 Hz, $J_{3',4'}$ = 6.0 Hz), 5.91 (t, H-2′, J = 4.6 Hz), 7.2–8.0 (m, aromatics). Anal. Calcd for $C_{30}H_{25}NO_8$: C, 68.31; H, 4.78; N, 2.66. Found: C, 68.28; H, 4.77; N, 2.58.

2-(Phenyldiazo)-4-(2,3,5-tri-*O*-benzoyl-α-D-ribofuranosyl)acetoacetonitrile (13a) and 2-(Phenyldiazo)-4-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)acetoacetonitrile (13b). Compound **12** (0.13 g, 0.25 mmol) was dissolved in a mixture of ethanol (10 mL), sodium acetate (0.1 g), and water (1 mL). This mixture was cooled to 5 °C and treated dropwise with a 0.44 M of benzenediazonium chloride (0.8 mL). The resulting yellow mixture was stirred for 1 h. Methylene chloride (50 mL) was added to the mixture, and the organic layer was separated, washed with saturated sodium bicarbonate solution (2 × 10 mL) and with a saturated sodium chloride solution (2 × 10 mL), and then dried over magnesium sulfate. Filtration and evaporation of the filtrate afforded a semisolid which was a mixture of compounds **13a** and **13b**, 0.16 g (100%). Column chromatography (silica gel, 30 g, 3 cm i.d. column, solvent system f) was used to separate the anomers **13a** and **13b** which were isolated after pooling and evaporation of the appropriate fractions (TLC, solvent system f). The α/β ratio (**13a**/**13b**) was essentially the same as that of the starting material **12**.

Compound 13a: yellow oil; R_f 0.13 (solvent system g); ^{1}H NMR (360 MHz, $CDCl_3$) δ 3.29 (m, H-4a, H-4b), 4.47 (m, H-4′), 4.60 (m, H-5′a, H-5′b), 5.01 (m, H-1′), 5.78 (dd, H-3′), 5.94 (dd, H-2′), 7.2–8.0 (m, 19, aromatic), 14.63 (s, NH). Anal. Calcd for $C_{36}H_{29}N_3O_8$: C, 68.46; H, 4.63; N, 6.65. Found: C, 68.56; H, 4.70; N, 6.51.

Compound 13b: yellow needles: mp 159.0–160.5 °C; R_f 0.1 (solvent g); ^{1}H NMR (360 MHz, $CDCl_3$) δ 3.32 (m, H-4a, H-4b), 4.50–4.69 (m, H-5′a, H-5′b), 4.7–4.8 (m, H-1′, H-4′), 5.58 (dd, H-2′), 5.69 (pseudo t, H-3′), 7.2–8.1 (m, 19, aromatic), 14.63 (s, NH). Anal. Calcd for $C_{36}H_{29}N_3O_8$: C, 68.46; H, 4.63; N, 6.65. Found: C, 68.43;, H, 4.89; N, 6.32.

Acknowledgment. We are grateful to Mr. John Krauss for his valuable technical assistance.

Registry No. **1a**, 83023-37-4; **1b**, 82921-67-3; α-**2**, 83476-38-4; β-**2**, 83476-39-5; α-**3**, 50907-76-1; β-**3**, 50907-75-0; **3** acid chloride, 83572-02-5; α-**4**, 83476-40-8; β-**4**, 83540-89-0; **5a**, 50907-77-2; **5b**, 50907-78-3; α-**6**, 83486-30-0; β-**6**, 83476-41-9; **7a**, 83476-42-0; **7b**, 83476-43-1; α-**8**, 83476-44-2; β-**8**, 83476-45-3; α-**9**, 83476-46-4; β-**9**, 83476-47-5; α-**10**, 66358-88-1; β-**10**, 66358-89-2; α-**11**, 83476-48-6; β-**11**, 83540-90-3; **12a**, 83476-49-7; **12b**, 83476-50-0; **13a**, 83476-51-1; **13b**, 83542-11-4; 1-*O*-acetyl-2,3,5-tri-*O*-benzoyl-β-D-ribofuranose, 6974-32-9; allyltrimethylsilane, 762-72-1; guanidine carbonate, 3425-08-9; *tert*-butyl cyanoacetate, 1116-98-9; cyanoacetic acid, 372-09-8; benzenediazonium chloride, 100-34-5.

Secondary α-Deuterium Kinetic Isotope Effects in Solvolyses of Ferrocenylmethyl Acetate and Benzoate in Ethanol[1a]

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Secondary α-deuterium kinetic isotope effects (KIE) in solvolyses of ferrocenyldideuteriomethyl acetate and benzoate were determined in 96% (v/v) ethanol, at 25 °C, as k_H/k_D = 1.24 and 1.26, respectively. The KIEs were also determined in the presence of 0.1 mol dm^{-3} lithium perchlorate: the k_H/k_D values were 1.23 and 1.22 for acetate and benzoate complexes, respectively. The maximum KIE for the C–O bond cleavage of a primary substrate is as large as, or larger than, that of secondary derivatives, which is estimated to be 1.23 per deuterium. The measured KIE of about 12% per D therefore represents a strongly reduced effect relative to its maximum. The solvolyses exhibit "a special salt effect". This effect indicates the presence of solvent-separated ion pairs and the return to tight pairs. As the maximum KIE is expected in solvolyses involving transformation of one type of ion pair into another, the strongly reduced α-D KIE supports the structure involving direct participation of electrons that in the ground state are localized at the iron atom. The alkyl–oxygen cleavage is accompanied by 10–15% acyl–oxygen cleavage.

The structure and stability of the α-ferrocenyl carbocations have been extensively studied,[2,3] but the structure of the ferrocenylmethyl cation ($FcCH_2^+$) is still a subject of debate. The dilemma is whether the electrons involved

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[1] (a) Taken from the Ph.D. thesis (in preparation) by D. Šutić, to be submitted to the Faculty of Pharmacy and Biochemistry, University of Zagreb; (b) University of Sarajevo, Sarajevo; (c) University of Zagreb.

[2] Uršič, S.; Ašperger, S. *J. Inorg. Nucl. Chem.* **1979**, *41*, 1329 and references therein.

0022-3263/82/1947-5120$01.25/0

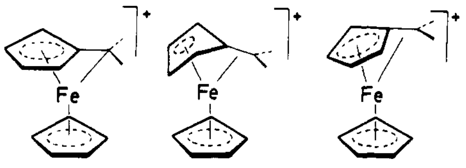

Figure 1. Possible structures of ferrocenylcarbenium ion involving a direct ion participation (Fe–C_{exo} bond formation).

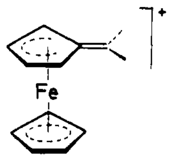

Figure 2. Possible structure of ferrocenylcarbenium ion involving conjugation with π system.

in its stability are those that in the ground state are localized at the iron atom[2,4] (Figure 1) or are those from iron–carbon bonds[5] (Figure 2). (There is also a possibility that both modes of stabilization are involved.)

Secondary α-deuterium kinetic isotope effects are a powerful tool in the elucidation of the mechanisms of nucleophilic substitutions. After the first observation of sizable α-deuterium effects in presumed carbenium ion processes reported independently by four different groups[6] and the observation of small effects in presumed S_N2-type nucleophilic displacements,[7] these effects were used to decide if a mechanism was a dissociative or a synchronous displacement (the $k_H/k_{\alpha\text{-D}}$ ratio in the latter case being around 1.00). The α-D effect on a limiting solvolysis is thought to be due principally to the lowering of the HCX bending force constant,[7] which would be expected to accompany the breaking of the C–X bond. The smaller effect in nucleophilic reactions may arise from a partially compensating gain of a new bending force produced by partial covalent attachement of the nucleophile to carbon. Therefore, the low α-D effect that we observed in solvolyses of $FcCH_2X$ might be due to partial covalent attachment of the nucleophile and/or to partial attachment of iron to the α-carbon at the reaction transition state. It is obvious that mechanistic conclusions regarding iron participation can be drawn only if this participation were practically the sole reason for the lowering of the measured isotope effect as compared with its maximum value.

Table I. Rates of Solvolyses of 0.01 mol dm^{-3} $FcCH_2OAc$ in 96% (v/v) Ethanol

T, K	HAc formed, mol %	$10^5k^H_{obsd}$, s^{-1}	$10^5k^H_{obsd}$, s^{-1} (mean)
288.16	83.2	0.493	0.505
	95.0	0.517	
298.16	84.4	1.96	1.95 ± 0.01
	83.4	1.94	(sem)^a
	81.5	1.98	
	81.4	1.94	
	80.7	1.92	
	88.3	1.94	
303.16	84.6	3.85	3.61
	90.8	3.44	
308.16	81.8	7.09	6.98
	80.9	6.88	

^{a} Standard error of the mean in all tables.

Table II. Rates of Solvolyses of 0.01 mol dm^{-3} $FcCD_2OAc$ in 96% (v/v) Ethanol^a

T, K	HAc formed, mol %	$10^5k^D_{obsd}$, s^{-1}	$10^5k^D_{obsd}$, s^{-1} (mean)
298.16	82.5	1.54	1.57 ± 0.01 (sem)
	83.7	1.59	
	90.7	1.58	
	93.3	1.56	

^{a} At 298.16 K the isotope effect k^H/k^D = 1.24 ± 0.01 (sem).

Table III. Rates of Solvolyses of 0.01 mol dm^{-3} $FcCH_2O_2CPh$ in 96% (v/v) Ethanol

T, K	HO_2CPh formed, mol %	$10^5k^H_{obsd}$, s^{-1}	$10^5k^H_{obsd}$, s^{-1} (mean)
288.16	83.5	1.22	1.22
	83.0	1.22	
298.16	80.9	3.96	3.99 ± 0.02 (sem)
	79.6	4.01	
	81.0	3.97	
	84.0	3.93	
	84.9	4.06	
	86.1	4.03	
	81.1	3.98	
303.16	82.1	7.11	7.20
	80.0	7.29	
308.16	84.5	12.35	12.40
	85.2	12.45	

Table IV. Rates of Solvolyses of 0.01 mol dm^{-3} $FcCD_2O_2CPh$ in 96% (v/v) Ethanol

T, K	HO_2CPh formed, mol %	$10^5k^D_{obsd}$, s^{-1}	$10^5k^D_{obsd}$, s^{-1} (mean)
298.16	84.2	3.21	3.16 ± 0.02 (sem)
	85.3	3.10	
	94.2	3.18	
	88.2	3.16	

In solvolyses, the maximum α-D isotope effect is observed when the rate-determining step involves the

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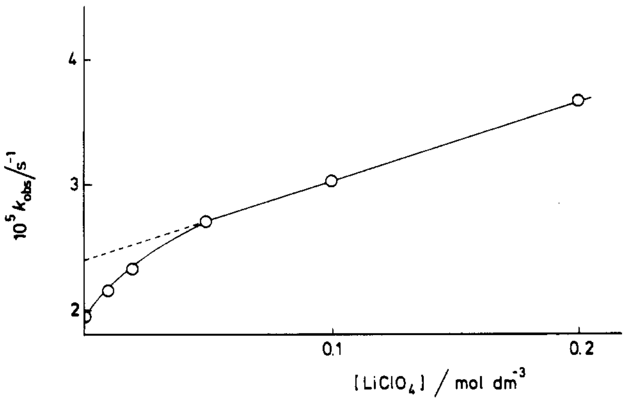

Figure 3. Salt effect of lithium perchlorate on solvolysis of 0.016 mol dm^{-3} ferrocenylmethyl acetate in 96 % (v/v) ethanol at 298 K.

transformation of one type of ion pair into another (or into free ions).[8,9] The solvolyses of ferrocenylmethyl acetate and benzoate in 96% v/v ethanol seems to meet these requirements. They are limiting-type solvolyses, the rate of which increases on addition of salts ("special salt effect"). This effect indicates the presence of the solvent-separated ion pairs and the return from these pairs.[10] Therefore we measured the α-D effect in solvolyses of ferrocenyldideuteriomethyl acetate and benzoate.

Results

Kinetic data of the rates of solvolyses of ferrocenylmethyl acetate and ferrocenyldideuteriomethyl acetate in 96% (v/v) ethanol are given in Tables I and II.

The parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were determined from the plots ln (k_{obs}/T) vs. $1/T$, which were good straight lines. The values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are 93.5 ± 2.5 kJ mol^{-1} and -22 ± 4 J mol^{-1} K^{-1}, respectively.

Solvolyses rates of ferrocenylmethyl benzoate and ferrocenyldideuteriomethyl benzoate in 96% (v/v) ethanol are given in Tables III and IV.

At 298.16 K the isotope effect $k^H/k^D = 1.26 \pm 0.01$, the value being almost equal to that for acetate solvolysis. The corresponding values for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are 83.2 ± 2.5 kJ mol^{-1} and -25 ± 4 J mol^{-1} K^{-1}, respectively, in reasonable agreement with those for acetate solvolysis.

Salt Effect in Solvolyses of Ferrocenylmethyl Acetate and Benzoate

Special Salt Effect. Figures 3 and 4 show plots of k_{obsd} vs. salt (lithium perchlorate) concentrations and reveal a combination of special[11,12] and normal[13] salt effects, similar to those previously noted in acetolysis of 2-*p*-anisyl *p*-toluenesulfonate[12] but about one-fourth the strength of the latter. Initial ionization of the substrate yields an "intimate" ion pair, in which the cation and anion lie in a common solvation shell, and internal return is a collapse of this pair. As the solvolysis proceeds, the "intimate" ion pair is converted to a solvent-separated ion pair, which may revert to an intimate ion pair or give products. Perchlorate intervenes, converting some of the solvent-separated ion pairs to solvent-separated perchlorate ion pairs.

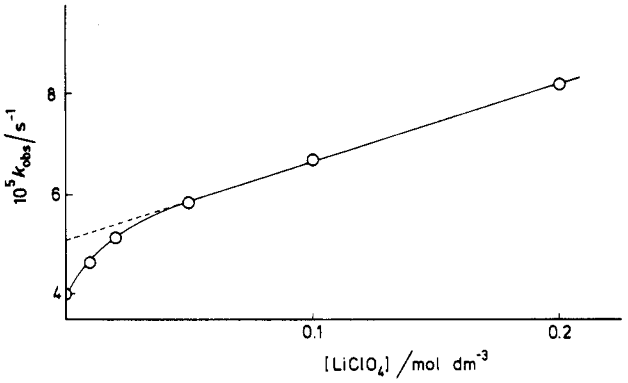

Figure 4. Salt effect of lithium perchlorate on solvolysis of 0.013 mol dm^{-3} ferrocenylmethyl benzoate in 96% (v/v) ethanol at 298 K.

From Figures 3 and 4 it can be seen that, with both the acetate and benzoate leaving groups, at perchlorate concentrations larger than 0.05 mol dm^{-3}, the external return of a solvent-separated ion pair to intimate ion pair is practically prevented. This is the reason why we also measured the kinetic deuterium isotope effects of ferrocenylmethyl acetate and benzoate solvolyses at 0.1 mol dm^{-3} perchlorate. Under such conditions the maximum α-D isotope effect should be definitely expected (see Discussion). A smaller isotope effect found than its possible maximum indicates that direct iron participation is involved.

In presence of 0.1 mol dm^{-3} LiClO$_4$ the α-D isotope effects, k_H/k_D, are found to be 1.23 ± 0.02 and 1.22 ± 0.02 for acetate and benzoate complexes, respectively. These values are only slightly lower than those determined without added perchlorate (1.24 ± 0.01 and 1.26 ± 0.01). Vitullo and Wilgis[14] studied salt effects and α-deuterium isotope effects in the solvolysis of benzal chlorides in 85% (v/v) dioxane–water mixtures. They observed that addition of perchlorate salts results in an initial rate acceleration due to prevention of ion-pair return. An increase in the α-D effect paralleled this rate increase, until a maximum α-D effect was reached when all significant return from solvent-separated ion pairs was prevented. The fact that the KIEs of acetate and benzoate complexes are practically the same in presence and absence of perchlorate suggests that the ion-pair return is small even in absence of perchlorate. Thus, one can expect but a small "special salt effect" as we indeed observed.

Common Ion Rate Depression Effect. The addition of sodium acetate (0.04 mol dm^{-3}) to a solution of ferrocenylmethyl acetate in 96% (v/v) ethanol reduced the reaction rate about 7-fold. At 298.16 K the rate constant is 2.73×10^{-6} s^{-1}, while in absence of extra added acetate ion the rate constant is 1.95×10^{-5} s^{-1} (see Table I). A calculation similar to that used by Swain[15] for the common-ion effect of chloride ion on trityl chloride solvolysis shows that the ferrocenylcarbonium ion reacts with acetate 3050 times as rapidly as it does with ethanol.

Discussion

In a previous paper[2] we reported that the α-deuterium kinetic isotope effect (k_H/k_D) in solvolysis of (ferrocenyldideuteriomethyl)trimethylammonium iodide was 1.06

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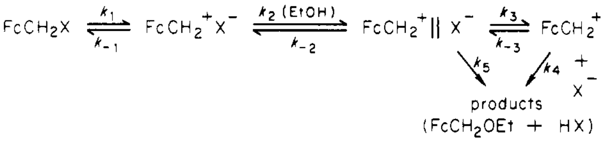
at 80 °C (about 3% per D). In the present work we found a significantly larger effect of 12% per D. Although both effects are much smaller than the theoretical maxima, the much lower value for the nitrogen leaving group is somewhat unexpected. It has been estimated that maximum α-D effects for nitrogen and oxygen leaving groups have similar magnitudes.[2] A possible explanation of the apparent discrepancy between the 3% and 12% D effects might be that a direct displacement reaction competes with solvolysis. This possibility comes to mind because the reaction center is primary and the solvent (water) relatively nucleophilic, while the leaving group is uncharged. It is interesting to note that the secondary α-deuterium isotope effects in the reaction of (2-phenylethyl)trimethylammonium ion by hydroxide ion in aqueous solution and by ethoxide ion in ethanol[16] amounts to only 2–3%. The corresponding ^{15}N primary kinetic isotope effect was found[17] to be less than one-third of the theoretical maximum effect (3.2%), revealing still appreciable carbon–nitrogen bonding in the transition state, and therefore a low α-D effect. Recently the secondary α-deuterium kinetic isotope effect in reaction of ferrocenylmethyl carbinol with pyridinium hydrochloride in aqueous solution was found[18] to be 14% per deuterium, but because of appreciable C–O binding in the reaction transition state no mechanistic conclusions regarding iron participation could be drawn.

It was already pointed out that the maximum α-D effect is observed in solvolyses when the rate-determining step involves transformation of one type of ion pair into another or into free ions.[7,19]

With secondary substrates the magnitude of the maximum effect is typical for a particular leaving group and is, e.g., 1.15 for chlorides and 1.23 for sulfonate esters.[7,8] The corresponding values for reactions of primary alkyl derivatives are difficult to estimate because they normaly do not solvolyze by the limiting dissociative mechanism. Calculations[19] and experimental results[20,21] support the idea that the magnitude of the isotope effect (per D) might be larger with the primary derivatives than with the secondary ones. For example, the ethanolysis of cyclopropylcarbinyl benzenesulfonate proceeds without internal rearrangement and with an α-D isotope effect of 20% per D.[21] It is reasonable to assume that this reaction might proceed without internal return since such return is invariably accompanied by rearrangement.[19] For secondary substrates it has been demonstrated[22] that limiting solvolyses, proceeding without internal return, show α-D effects *smaller* than the characteristic maximum. Therefore, it is estimated that the characteristic upper limit of the α-D effect for the cleavage of the C–O bond in solvolyses of primary substrates is probably as large or larger than that of secondary derivatives (1.23). Consequently the measured isotope effect of 12% per D for ferrocenylmethyl acetate and benzoate, involving transformation of intimate ion pair into solvent-separated ion pair (and free ion), represents a strongly reduced effect from its maximum and supports the structure depicted in Figure 1.

The reactions involved can be presented by equilibria 1 (X^- = acetate or benzoate).



(1)

In eq 1 steps 4 and 5 are most probably not reversible as the returns from $FcCH_2OEt$ are hydrogen ion catalyzed, and the concentrations of hydrogen ion in alcoholic solutions of the acids (acetic or benzoic) are very small. If $FcCH_2OEt$ is a stable reaction product indeed and the alkyl–oxygen cleveage were not accompanied by acyl–oxygen cleavage, the solvolysis should yield 1 mol of acid, HX, per mol of $FcCH_2X$. This is especially true when lithium perchlorate is present and the returns in steps 2 and 3 are prevented. The experiments showed (Tables I–IV) that about 85–90 mol % of corresponding acids (HX) are formed, even in presence of large excess (0.2 mol dm^{-3}) of lithium perchlorate. We believe that the smaller yield of acetic and benzoic acids is caused by acyl–oxygen fission, accompanying alkyl–oxygen fission. Nugent et al. also observed a 5–7% smaller infinity titer in the solvolysis of β-ferrocenylalkyl tosylates.[4e] They explained these results as being due to large standard deviations. As k_H/k_D in the acyl–oxygen cleavage is most probably very near unity, the measured k_H/k_D relates practically completely to S_N1 alkyl–oxygen cleavage.

The steady-state approximation applied to the short-lived intimate ion pair $FcCH_2^+X^-$, in presence of perchlorate, leads to the eq 2.

$$-d[FcCH_2X]/dt = \frac{k_1k_2}{k_{-1} + k_2}[FcCH_2X] \qquad (2)$$

If k_2 is neglected relative to k_{-1} (rate of diffusion with charge separation is about 10–100 times slower than the normal diffusion,[23] so that k_2 is probably 10^9–10^{10} s^{-1}) eq 3 is obtained.

$$-d[FcCH_2X]/dt = K_1k_2[FcCH_2X] \qquad (3)$$

The α-D isotope effect is then given by eq 4.

$$\frac{k^H}{k^D} = \frac{K_1{}^Hk_2{}^H}{K_1{}^Dk_2{}^D} \simeq \frac{K_1{}^H}{K_1{}^D} \qquad (4)$$

This should be especially so in the presence of lithium perchlorate when steps 2 and 3 in eq 1 become practically irreversible.

The rate of solvolysis of 0.015 mol dm^{-3} ferrocenylmethyl benzoate in absolute ethanol, containing 0.02% water, at 298.16 K, was measured, and the rate constant was determined as 1.47×10^{-5} s^{-1}. This value is 2.7 times smaller than that determined in 96% (v/v) ethanol. The solvent effect on rate is about what one would expect for a unimolecular nucleophilic substitution.[24] The infinity titer in absolute ethanol and that in 96% (v/v) ethanol were the same, which suggests that the change of solvent dielectric constant is of primary importance, influencing similarly the rates of both the alkyl- and acyl–oxygen fissions, and that water molecules in 96% (v/v) ethanol are not free for chemical reactions. Namely, water as the nucleophile yields acetic acid in both types of cleavages, while ethanol as nucleophile yields acetic acid in alkyl–oxygen cleavage only. The slightly negative entropies of activation of solvolyses of ferrocenylmethyl acetate (−22

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J mol^{-1} K^{-1}) and of ferrocenylmethyl benzoate (−25 J mol^{-1} K^{-1}) are generally expected in reactions proceeding with neighboring group participation. For example, it has been concluded that the assisted solvolyses tend to have $\Delta S^{\ddagger}$ of about −30 J mol^{-1} K^{-1}, as it is the case in formolysis of 2-phenylethyl tosylate,[25] where $\Delta S^{\ddagger} = -40$ J mol^{-1} K^{-1}. In the case of more reactive 2,2-dimethyl-2-phenylethyl tosylate $\Delta S^{\ddagger}$ is −31, −23, and −26 J mol^{-1} K^{-1} in ethanol, acetic acid, and formic acid, respectively.[25]

Experimental Section

Preparations. Ferrocenylmethyl acetate was obtained from (ferrocenylmethyl)trimethylammonium iodide, via carbinol,[26] by the method previously published;[27] mp 68–69 °C; ν(CO) 1750 cm^{-1}.

Anal. Calcd for $C_{13}H_{14}O_2Fe$: C, 60.28; H, 5.73; Fe, 21.58. Found: C, 60.50; H, 5.43; Fe, 21.32 (gravimetrically).

Ferrocenyldideuteriomethyl acetate was prepared in the same way as the undeuterated compound, but by using D_3PO_4, NaOD, CH_3COOD, D_2O (Merck, 99,8 %), and bis(dimethylamino)dideuteriomethane[28] instead of undeuterated material. The NMR spectra showed that the deuteration was essentially complete.

Ferrocenylmethyl benzoate was prepared from the corresponding carbinol with benzoyl chloride in pyridine by using a general procedure;[29] mp 130–132 °C; ν(CO) 1745 cm^{-1}.

Anal. Calcd for $C_{18}H_{16}O_2Fe$: C, 67.52; H, 5.04; Fe, 17.44. Found: C, 67.31; H, 5.27; Fe, 17.22.

Ferrocenyldideuteriomethyl benzoate was prepared from deuterated carbinol as described for the undeuterated compound. All preparations were carried out in an argon atmosphere to avoid the formation of ferricynium salts.[30]

The chemicals used, including deuterated compounds, were from Merck and of analytical purity. D_2CO, needed for preparation of bis(dimethylamino)dideuteriomethane[28] was supplied as 30% (v/v) solution of 99% D_2CO in D_2O (99.8%), stabilized by deuterated methanol.

Kinetics. Solvolyses of ferrocenylmethyl acetate and benzoate as well as solvolyses of their deuterated analogues were carried out in 96% (v/v) ethanol. The weighed quantity of the complex was dissolved in ethanol thermally equilibrated at desired temperature (±0.02 °C). Aliquots were withdrawn at suitable intervals, quenched by 10-fold dilution with ice-cold ethanol, and titrated with standardized sodium hydroxide solution, with phenol red indicator. A stream of argon was passed through the quenched solution for about 5 min to eliminate carbon dioxide and during titration only over the surface of the reaction solution. First-order rate constants were calculated by using a nonlinear regression analysis computer program[31] on a PDP 8/e computer.

Apparatus. ^1H NMR spectra were recorded on a Varian 60 Mc ^1H NMR spectrometer, and IR spectra on a Perkin-Elmer 457 IR spectrophotometer.

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Registry No. D_2, 7782-39-0; $FcCH_2OAc$, 12300-24-2; $FcCH_2O_2CPh$, 12300-31-1.

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Cationic Derivatives of Bicyclo[4.2.1]nona-2,4,7-triene as Model Systems for Ground-State Möbius Aromaticity[†]

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A number of syn-C_{10} carbocations of bicyclo[4.2.1]nona-2,4,7-triene 1 are described, furnishing possible model systems for the investigation of ground-state Möbius aromaticity. Sign inversion, necessary for 4-π-electron aromaticity, is realized by a simple orientation of the C_{10} p orbital which is homoconjugated with $C_{2,5}$. ^{13}C and ^1H NMR spectroscopy suggest that the empty orbital at C_{10} is orientated perpendicularly with respect to the mirror plane of the cations. The saturated analogues of these cations also adopt this configuration. The chemical shift differences between the unsaturated cations and the saturated derivatives suggest a charge delocalization via Möbius aromaticity.

A concept which has been of special interest for organic chemists is the Hückel rule,[1] which says that for ground-state molecules with a cyclic array of atomic orbitals, $4n + 2$ electrons result in aromaticity and thermodynamical stability. Fundamental in Hückel's reasoning is the large energy difference between the ground-state and the excited state(s) in a ring with $4n + 2$ electrons, whereas $4n$ electrons result in a small energy separation. The same is also true for a cyclic array of orbitals with $4n$ and $4n + 2$ electrons, respectively, when this interchange is accompanied with an odd number of sign inversions for the orbitals in the ring.[2] In the latter case, we are generally speaking of Möbius aromaticity: $4n$ electrons result in aromaticity. By use of simple MO calculations, the Möbius aromaticity concept has been explored for a variety of reactions, which are commonly known as Woodward–Hoffmann reactions.[3,4] Ground-state Möbius aromaticity has never been observed as a consequence of the steric strain, which imposes a sign inversion on a small cyclic

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