High Secondary α-Deuterium Kinetic Isotope Effect in the Acetolysis and Formolysis of Dideuterioferrocenylmethyl Benzoate†

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Acetolysis and formolysis of dideuterioferrocenylmethyl benzoate exhibit large secondary α-deuterium kinetic isotope effects and an abnormal temperature dependence. In the presence of $LiClO_4$ (*ca.* 0.1 mol dm^{-3}), which prevents the reversion from solvent-separated to contact ion-pairs, k_H/k_D at 25 °C amount to 1.53 ± 0.02 (acetolysis) and 1.48 ± 0.03 (formolysis). In the presence of $LiClO_4$ the ratios of Arrhenius pre-exponential factors, A_H/A_D, are significantly less than unity and amount to 0.49 ± 0.01 (acetolysis) and 0.38 ± 0.04 (formolysis). In the absence of $LiClO_4$ the A_H/A_D ratios are much smaller (0.02 both in acetolysis and formolysis). We suggest that these surprisingly low values result from a change in rate-determining step over the temperature range, from formation of the solvent-separated ion-pair at low temperatures to reaction of the dissociated carbocation with solvent at the highest temperatures. Whether tunnelling plays any role in these solvolyses is discussed.

The secondary α-deuterium isotope effect (KIE) in acetolysis of dideuterioferrocenylmethyl benzoate was previously determined by us[1] at 25 °C as $k_H/k_D = 1.50$ [22.5% per D (geometric mean)]. This appeared to be one of the largest KIEs observed for carbon–oxygen cleavage.[2] The solvolysis exhibited a special salt effect and a common-ion rate depression effect, indicating the presence of solvent-separated ion-pairs and the return to tight ion-pairs. The high value of the KIE strongly suggested that the acetolysis is a limiting dissociative process with a carbonium ion-like transition state stabilized mainly by conjugation with the π-system of the pentadienyl ring. This result was compared with a previously-determined KIE of only 11.4% per D in ethanolysis of dideuterioferrocenylmethyl acetate and benzoate, respectively,[3] where the stabilization of the transition state probably involves some Fe–C_{exo} bond formation. We now report that the k_H/k_D of formylysis is 1.48 ± 0.03 at 25 °C, a value slightly lower than that of acetolysis (1.53 ± 0.02).

Both acids are roughly equally poor nucleophiles but good ionizing solvents, while ethanol is a relatively good nucleophile but poorly ionizing.[4,5] The high KIE, both in acetolysis and formolysis, prompted a study of the temperature dependence of the solvolysis rates and of the KIE in order to see if tunnelling might be operative. That tunnelling can contribute to secondary isotope effects is supported by model calculations, which predict appreciable tunnel corrections when the bending motions of the non-transferred proton are coupled with the stretching motion of the transferred proton.[6] The calculations also predict that tunnelling can lead to the same sort of abnormal temperature dependence as is observed for primary isotope effects; the ratio of Arrhenius pre-exponential factors A_H/A_D (or A_H/A_T) is significantly less than unity. An experimental example of this behaviour is the reaction of $PhCHTCH_2NMe_3^+$ with EtO^-, which gives $A_H/A_T = 0.705 \pm 0.024$.[7]

Tunnelling is expected to be diminished when an atom heavier than the proton is transferred, and $(k_H/k_T)_{sec}$ is in fact less when deuterium is transferred than when protium is transferred.[7] One might expect that tunnelling would not be important in the solvolyses of ferrocenylmethyl esters because oxygen (mass 16) is now the transferred atom. The system appeared ideal to provide a critical test because the isotope effect is large, and it is easier to measure the temperature dependence of a large than of a small isotope effect.

Table 1 Rates of acetolysis of 5 × 10^{-4} mol dm^{-3} ferrocenylmethyl and dideuterioferrocenylmethyl benzoate in glacial acetic acid in the presence of 0.1 mol dm^{-3} $LiClO_4$[a]

T/K	$k^H{}_{obs}$/ 10^{-4} s^{-1}	$k^D{}_{obs}$/ 10^{-4} s^{-1}	$(k^H/k^D)_{obs}$	% KIE per α-D (geometric mean)
289.16	41.33 ± 0.88	26.01 ± 0.25	1.59 ± 0.02	26.0 ± 1.2
293.16	49.44 ± 0.49	31.66 ± 0.78	1.56 ± 0.03	25.0 ± 1.3
298.16	61.70 ± 0.35	40.25 ± 0.93	1.53 ± 0.02	23.8 ± 1.2
303.16	76.00 ± 1.81	50.50 ± 1.23	1.50 ± 0.03	22.5 ± 1.5
313.16[b]	114.26	79.36	1.44	20.0

[a] Each rate constant is the mean of three independent measurements. [b] Extrapolated values for comparison with measured values in formolysis.

Table 2 Rates of formolysis of 3.2 × 10^{-4} mol dm^{-3} ferrocenylmethyl and dideuterioferrocenylmethyl benzoate in anhydrous formic acid in the presence of 0.07 mol dm^{-3} $LiClO_4$[a]

T/K	$k^H{}_{obs}$/ 10^{-4} s^{-1}	$k^D{}_{obs}$/ 10^{-4} s^{-1}	$(k^H/k^D)_{obs}$	% KIE per α-D (geometric mean)
288.16	8.90 + 0.23	5.75 ± 0.11	1.55 ± 0.03	24.4 ± 1.8
293.16	11.66 ± 0.31	7.80 ± 0.08	1.50 ± 0.03	22.5 ± 1.6
298.16	14.50 ± 0.55	9.79 ± 0.03	1.48 ± 0.03	21.7 ± 1.9
313.16	26.41 ± 0.08	19.16 ± 0.38	1.38 ± 0.02	17.5 ± 1.0

[a] Each rate constant is the mean of three independent measurements.

Results

Tables 1 and 2 contain the rates of acetolysis in glacial acetic

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† Taken from the thesis to be submitted by Z. Kukrić in partial fulfilment of the requirements for the Ph.D. degree at the University of Zagreb.

Table 3 Energy and entropy parameters for acetolysis and formolysis of 5×10^{-4} mol dm^{-3} ferrocenylmethyl and dideuterioferrocenylmethyl benzoate in the presence of $LiClO_4$. Reaction conditions as described in Tables 1 and 2

	Acetolysis		Formolysis	
	α-H_2	α-D_2	α-H_2	α-D_2
E_a/kJ mol^{-1}	31.7 ± 0.1	34.6 ± 0.1	32.3 ± 0.9	35.6 ± 1.1
$\Delta S^‡$/J mol^{-1} K^{-1}	−189 ± 1.5	−183 ± 1.8	−199 ± 1.6	−191 ± 1.7
A/s^{-1}	2256 ± 110	4565 ± 240	642 ± 50	1697 ± 170
A_H/A_D	0.49 ± 0.01		0.38 ± 0.04	

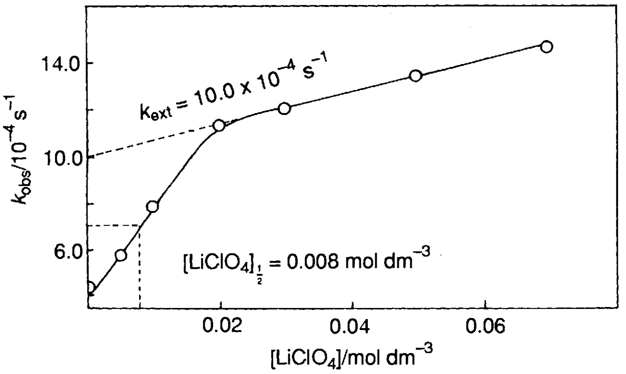


Fig. 1 A plot of special and normal salt effects of lithium perchlorate on solvolysis of 3.2×10^{-4} mol dm^{-3} ferrocenylmethyl benzoate in anhydrous formic acid at 298.16 K

acid and formolysis in anhydrous formic acid of ferrocenylmethyl and dideuterioferrocenylmethyl benzoate (5×10^{-4} and 3.2×10^{-4} mol dm^{-3}, respectively), in the presence of $LiClO_4$ (0.1 in acetolysis and 0.07 mol dm^{-3} in formolysis). Fig. 1 reveals that the formolysis (practically the same effect is observed in acetolysis as well)[1] exhibits a strong special salt effect[8] in combination with a normal salt effect.[9] The initial ionisation of the ferrocenylmethyl benzoate yields a tight (contact) ion-pair which then converts to a solvent-separated ion-pair. Fig. 1 reveals that the special salt effect is completed at *ca.* 0.02 mol dm^{-3} $LiClO_4$. The concentrations of $LiClO_4$ used in acetolysis (0.1 mol dm^{-3}) and in formolysis (0.07 mol dm^{-3}) therefore assured complete prevention of the reversion of solvent-separated to tight ion-pairs.

Data from Tables 1 and 2 enabled the determination of the energy and entropy parameters for acetolysis and formolysis (in the presence of $LiClO_4$). Eqns. (1)–(3) were used.

$$\ln \frac{k_{obs}}{T} = \frac{\Delta H^‡}{RT} + \frac{\Delta S^‡}{R} + \ln \frac{k_B}{h} \qquad (1)$$

$$\ln \frac{k^H_{obs}}{k^D_{obs}} = \frac{E^D_a = E^H_a}{RT} + \ln \frac{A^H}{A^D} \qquad (2)$$

$$\ln k_{obs} = \frac{-E_a}{RT} + \ln A \qquad (3)$$

The ratios of Arrhenius pre-exponential factors, A_H/A_D, computer calculated from eqn. (2), have smaller standard deviations than those calculated from eqn. (3). On the other hand, eqn. (3) enables the determination of individual values of E_a and A for deuteriated and undeuteriated species. The results are collected in Table 3. The data in Tables 1 and 2 show that the KIE is somewhat smaller in formolysis than in acetolysis. One might have expected just the opposite because formic acid is a better ionizing solvent than acetic acid.[4,5] Tables 1 and 2 also reveal that the isotope effect decreases appreciably with increasing temperature. Table 3 shows that the differences in energies of activation for the reactions of deuteriated and undeuteriated species are almost equal in acetolysis and formolysis (~3 kJ mol^{-1}). The same holds for entropies of activation [$\Delta(\Delta S^‡)$ *ca.* 6–7 J mol^{-1} K^{-1}].

The A_H/A_D values of 0.49 ± 0.01 for acetolysis and 0.38 ± 0.04 for formolysis in the presence of $LiClO_4$ are already of a magnitude (<0.5) considered indicative of tunnelling when hydrogen transfer is rate determining,[10,11] and are lower than the A_H/A_T values (~0.7) that have been found for secondary tritium isotope effects in elimination reactions and attributed to tunnelling.[7] We will return to this point in the Discussion.

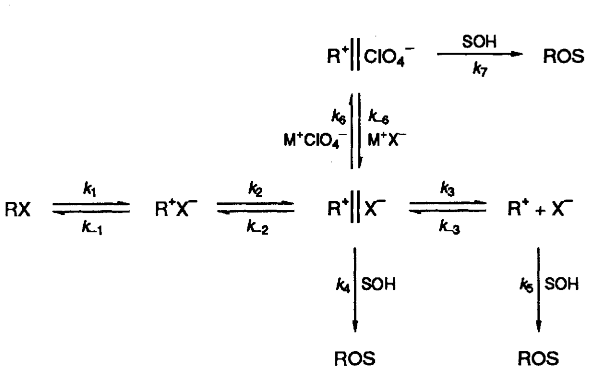
Both acetolysis[1] and formolysis show a strong common ion rate-depression effect.[12] In Fig. 2 a plot of $k_{obs}{}^0/k_{obs}$ *vs.* $\alpha[X^-] + 1$ is given for formolysis where $k_{obs}{}^0$ and k_{obs} are the rates in the absence and in the presence of common ion X^-, respectively.

Entirely different A_H/A_D values are obtained when acetolysis and formolysis are carried out in the absence of $LiClO_4$: A_H/A_D is 0.02, both for acetolysis and formolysis. The decrease of the KIE with increase of temperature is much larger in the absence than in the presence of $LiClO_4$. In acetolysis in the presence of $LiClO_4$, the KIE per D varies between 26.0% (16 °C) and 20.0% (40 °C), while in the absence of $LiClO_4$ the KIE varies between 23.3% (20 °C) and 9.1% (40 °C). (In the absence of $LiClO_4$ the temperature interval had to be narrower because pure glacial acetic freezes at 16.6 °C.) In formolysis in the presence of $LiClO_4$, the KIE varies between 24.4% (15 °C) and 17.5% (40 °C), while in the absence of $LiClO_4$ over the same temperature interval, the KIE varies between 29.9% and 10.1%, respectively. Tables 1, 2, 4 and 5 contain these results. From Table 6 we can see that the differences in energies of activation between deuteriated and undeuteriated species are now 10.6 kJ mol^{-1} both in acetolysis and formolysis, while in the presence of $LiClO_4$ these differences were *ca.* 3 kJ mol^{-1} for both solvolyses. The differences in entropies of activation are also much larger in the absence of $LiClO_4$ (~35 J mol^{-1} K^{-1}, Table 6).

Discussion

Values of A_H/A_D for primary deuterium isotope effects that are very much smaller than unity have been known for some time, and have usually been explained as a consequence of tunnelling.[10] More recently, values below unity have been found for secondary deuterium isotope effects and have been given a similar explanation.[7] The values that we find in the absence of $LiClO_4$, however, are very much below what has previously been found or might be expected for secondary effects. In this case there seems no reasonable alternative to mechanistic complexity as an explanation. The values in the presence of $LiClO_4$ are much less extreme, but still sufficiently abnormal to require some discussion.

The unusual temperature dependence in the absence of lithium perchlorate can be understood, at least qualitatively, in terms of the Winstein mechanism for solvolysis (Scheme 1).[13]



Scheme 1

In the presence of lithium perchlorate we can assume that the solvent-separated ion-pair reacts rapidly by the k_6 and k_7 route to give solvolysis product. The more normal temperature dependence under these conditions suggests that this is at least the major pathway. That A_H/A_D is still significantly below unity may mean that this is not the sole route followed, or that some tunnelling occurs. In this interpretation, the dissociation of the intimate ion-pair (the k_2 step) is mainly or entirely rate determining.

In the absence of lithium perchlorate, it is evident from the

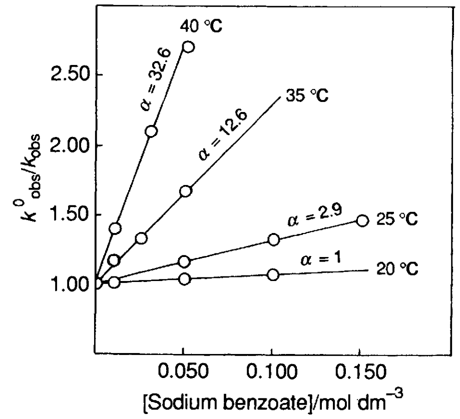


Fig. 2 Common-ion rate depression in formolysis of 3.2×10^{-4} mol dm^{-3} ferrocenylmethyl benzoate. Observed rates in absence of common ion, $k_{obs}/10^{-4}$ s^{-1}, at 20, 25, 30 and 40 °C amount to 2.64 ± 0.15, 4.13 ± 0.08, 7.29 ± 0.31, and 19.04 ± 0.64, respectively.

Table 4 Rates of acetolysis of 5×10^{-4} mol dm^{-3} ferrocenylmethyl and dideuterioferrocenylmethyl benzoate in glacial acetic acid in the absence of $LiClO_4$[a]

T/K	$k^H_{obs}/10^{-4}$ s^{-1}	$k^D_{obs}/10^{-4}$ s^{-1}	$(k^H/k^D)_{obs}$	% KIE per α-D (geometric mean)	$(k^H/k^D)_{cal}$ with $LiClO_4$[b]
293.16	3.42 ± 0.03 4	2.25 ± 0.04 3	1.52 ± 0.02	23.3 ± 0.1	1.56
296.16	5.09 ± 0.03 3	3.35 ± 0.08 3	1.52 ± 0.02	23.3 ± 1.2	1.54
298.16	6.24 ± 0.08 8	4.16 ± 0.07 6	1.50 ± 0.02	22.5 ± 1.1	1.53
300.16	7.70 ± 0.13 3	5.66 ± 0.05 3	1.36 ± 0.02	16.6 ± 0.9	1.52
304.16	13.33 ± 0.40 3	9.83 ± 0.30 3	1.36 ± 0.04	16.6 ± 2.0	1.49
306.16	14.81 ± 0.20 3	11.50 ± 0.20 2	1.29 ± 0.02	13.5 ± 1.0	1.48
308.16	17.99 ± 0.15 2	14.66 ± 0.22 2	1.23 ± 0.02	10.9 ± 0.8	1.47
313.16	32.21 ± 0.90 3	27.08 ± 0.71 3	1.19 ± 0.04	9.1 ± 1.9	1.44

[a] Number of measurements given in second row. [b] Values calculated from the Arrhenius parameters for reactions in the presence of $LiClO_4$.

Table 5 Rates of formolysis of 3.2×10^{-4} mol dm^{-3} ferrocenylmethyl and dideuterioferrocenylmethyl benzoate in anhydrous formic acid in the absence of $LiClO_4$[a]

T/K	$k^H_{obs}/10^{-4}$ s^{-1}	$k^D_{obs}/10^{-4}$ s^{-1}	$(k^H/k^D)_{obs}$	% KIE per α-D (geometric mean)	$(k^H/k^D)_{cal}$ with $LiClO_4$[b]
288.16	1.39 ± 0.08 3[a]	0.83 ± 0.05 2	1.68 ± 0.08	29.9 ± 3.0	1.55
293.16	2.45 ± 0.15 4	1.53 ± 0.07 2	1.60 ± 0.07	26.6 ± 3.0	1.51
298.16	4.13 ± 0.22 7	2.77 ± 0.07 5	1.49 ± 0.06	22.1 ± 2.9	1.47
303.16	7.29 ± 0.30 2	5.24 ± 0.20 2	1.39 ± 0.05	16.8 ± 2.5	1.44
307.16	10.90 ± 0.25 2	8.65 ± 0.05 2	1.26 ± 0.02	12.2 ± 1.2	1.42
310.16	14.70 ± 0.62 3	11.79 ± 0.23 3	1.25 ± 0.05	11.7 ± 3.0	1.40
313.16	19.04 ± 0.80 2	15.71 ± 0.62 2	1.21 ± 0.06	10.1 ± 2.8	1.38

[a] Number of measurements given in second row. [b] Values calculated from the Arrhenius parameters for reactions in the presence of $LiClO_4$.

Table 6 Energy and entropy parameters for acetolysis and formolysis of 5 × 10^{-4} mol dm^{-3} ferrocenylmethyl and dideuterioferrocenylmethyl benzoate in the absence of $LiClO_4$. Reaction conditions as described in Tables 4 and 5

	Acetolysis		Formolysis	
	α-H_2	α-D_2	α-H_2	α-D_2
E_a/kJ mol^{-1}	84.11 ± 1.2	94.7 ± 0.8	79.2 ± 0.7	89.8 ± 1.1
$\Delta S^{\ddagger}$/J mol^{-1} K^{-1}	−32.6 + 1.5	0.2 ± 0.2	−55 ± 2	−20.0 ± 2.0
A/s^{-1}	(3.68 ± 0.60) 10^{11}	(1.67 ± 0.05) 10^{13}	(3.16 ± 0.95) 10^{10}	(1.53 ± 0.60) 10^{12}
A_H/A_D	0.02 ± 0.01		0.02 ± 0.04	

common-ion effect that there is some return from the dissociated ions (the k_{-3} step), and that the product must at least in part be formed by the k_5 step. The return is strongly temperature dependent, being much more important at the more elevated temperatures. Over this temperature range, then, the mainly rate-determining step changes from k_2 at the lowest to k_5 at the highest temperature. A maximal secondary isotope effect is expected for the k_2 step because there is no covalent bonding to R^+, while a smaller isotope effect is expected for the k_5 step because a new covalent bond has started to form between R^+ and SOH. Thus the isotope effects under both sets of conditions are expected to be similar at the lower temperatures, but those in the absence of lithium perchlorate should be smaller at the higher temperatures than those in its presence.

There is an experimental inconsistency in this picture. The observed isotope effects in the absence of $LiClO_4$ along with those in its presence (calculated from the temperature dependences) are given in the fourth and sixth columns, respectively, of Tables 4 and 5. The comparison shows that the former are smaller at the higher temperatures and that the two sets of isotope effects are of comparable magnitude at the lower temperatures, except for the values in formolysis at 15 °C, which are significantly larger in the absence of $LiClO_4$ than in its presence. The above mechanism as stated implies that the isotope effects in the absence of lithium perchlorate should only be less than or equal to those in its presence. There is no reason to doubt the accuracy of the values at 15 °C, except that they are somewhat larger than would be expected from extrapolation of values at nearby temperatures. If these values are substantially correct, there must be some additional mechanistic complexity that we have not allowed for.

That a simple change in rate-determining step with temperature is not the whole story becomes still more likely when the quantitative implications are examined. If the only effect of temperature is on the ratio $k_{-3}[X^-]/k_5$ (Scheme 1), then to go from rate determination by the k_5 step at 40 °C to rate determination by the k_2 step at 15 °C implies that this ratio decrease from ~10 to ~0.1 over the temperature range. Such a change requires a very large difference in activation energies (E_5–E_{-3} ~ 140 kJ mol^{-1}) and an extremely low ratio of pre-exponential factors (A_{-3}/A_5 ~ 10^{-24}) to compensate. Differences of this magnitude seem unlikely. The temperature dependence of the common-ion effect leaves no room for doubt that the postulated change in rate-determining step is occurring. Temperature effects on other rates and equilibria in this system must, however, also be involved. Quantitative modelling of these effects is not possible given our present state of knowledge.

Finally, we might ask if it is reasonable to ascribe the moderately abnormal temperature dependence in the presence of $LiClO_4$ to tunnelling. The postulated rate-determining step in this case is the conversion of the contact ion-pair to the solvent-separated ion-pair, so the answer depends on whether motion of the α hydrogens contributes to the motion along the reaction coordinate.[7] If the α carbon is already planar in the contact ion-pair, it is difficult to see how such motion could contribute. If it is still non-planar in the contact ion-pair and becomes planar as the solvent separated ion-pair forms, then motion of the α hydrogens will contribute to the motion along the reaction coordinate, and a contribution of tunnelling is a possibility. It is also possible that k_2 is not wholly rate-controlling, in which case competition between it and another step could be responsible for the temperature dependence. In any event, it is clear that low A_H/A_D values cannot be taken as proof of tunnelling in the presence of mechanistic complexity.

Experimental

Preparations.—The chemicals used, including deuteriated compounds, were Merck, analytical grade. Deuteriated formaldehyde needed for the preparation of bis(dimethylamino)-dideuteriomethane[14] was supplied as a 30% (v/v) solution of D_2CO (95%) in D_2O (99.8%) stabilized by CD_3OD. The ferrocenylmethyl benzoate used was from a previously prepared batch.[1] Dideuterioferrocenylmethyl benzoate was prepared from the deuteriated alcohol in the same way as for the undeuteriated benzoate.[1] The ^1H NMR spectrum showed that deuteriation of the methylene group is practically complete. All preparations were carried out in an oxygen-free argon atmosphere to avoid formation of ferricenium salts.[15]

Kinetics.—Acetolysis of ferrocenylmethyl benzoate as well as its dideuteriated analogue were carried out in glacial acetic acid. Formolyses were performed in anhydrous formic acid. The kinetics were followed spectrophotometrically at 436 nm both in acetolyses and formolyses. In acetolysis 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 dm^3 mol^{-1} cm^{-1}, respectively). The difference was large enough for kinetic measurements in 10 cm cells. The kinetics of the formolyses can be followed more easily because the difference in molar absorptivities between benzoate and formate is somewhat larger than that between benzoate and acetate. The thermostatted absorption cell (25 ± 0.05 °C) was used as the reaction vessel. It was flushed several times with very pure argon (99.999%) further purified by passing over chromium(II) salts dispsersed on silica. The details of the apparatus for spectrophotometric measurements in oxygen-free argon have been described previously.[16]

Apparatus.—A Cary 219 instrument was used for spectral measurements. ^1H NMR spectra were recorded on a JEOL 60 MHz ^1H spectrometer. IR spectra were measured on a Perkin-Elmer 783 IR spectrophotometer.

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