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Acid-catalyzed hydrolysis of bridged bi- and tricyclic compounds. XXXVII. Kinetics and mechanisms of 1- and 3-acetoxynortricyclanes

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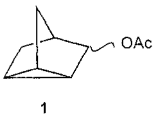
ABSTRACT: The disappearance of 3- and 1-acetoxynortricyclanes (1 and 2) in aqueous perchloric acid was followed by capillary gas chromatography at different temperatures and acid concentrations. According to the activation parameters, solvent deuterium isotope effects and parameters of excess acidity equations, the $A_{AC}2$ ester hydrolysis with two water molecules in the transition state is dominant at the lower acid concentrations studied (1–5.5 M $HClO_4$) and the Ad_E2 hydration of the cyclopropane ring is dominant at higher acid concentrations (6–8 M $HClO_4$) at 298 K. 3-Nortricyclanol (3) is formed via hydrolysis from 1, whose hydration products were not analyzed. 2-Norbornanone (4) is formed via both hydrolysis and hydration from 2. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: nortricyclanes; 2-norbornanone (norcamphor); kinetics; acid catalysis; excess acidity; ester hydrolysis; hydration; reaction mechanism

INTRODUCTION

The hydrolysis of 3-acetoxynortricyclane or 3-acetoxytricyclo[2.2.1.0^{2,6}]heptane **(1)** follows the $A_{AC}2$ mechanism (the acid-catalyzed bimolecular reaction via acyl-oxygen fission)[1,2] in 1 mol dm^{-3} $HClO_4$ in 60 vol.% dioxane–water, and variations in temperature, dioxane: water ratio (1 M $HClO_4$) or acid concentration (60% dioxane–water) do not alter the mechanism.[3] However, a comparison of the rate constants of protonation (hydration via the Ad_E2 or $A-S_E2$ mechanism) of the cyclopropane ring of 3-substituted nortricyclanes hints that the hydration may be observable in aqueous $HClO_4$.[4,5] An increase in acid concentration should increase the level of hydration and decrease that of the $A_{AC}2$ ester hydrolysis because of decreasing water activity. Therefore, the kinetics of 3-acetoxynortricyclane **(1)** and of its interesting isomer, 1-acetoxynortricyclane **(2)**, in which the substituent is situated on a cyclopropane carbon atom, were studied in this work in aqueous perchloric acid at different acid concentrations.



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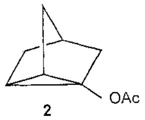

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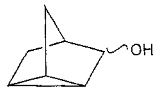

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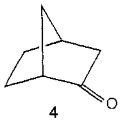

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EXPERIMENTAL

Materials. The syntheses of 3- and 1-acetoxynortricyclanes (**1** and **2**) have been presented previously.[6,7] The purities by gas chromatography (GC) were >99.5 and 97% (3% of 4-acetoxynortricyclane?), respectively. The acetates were identified from their ^{13}C NMR and GC–FTIR spectra.[5,6]

Kinetic measurements. The disappearance of the substrates in $HClO_4$(aq.) was followed by GC (with an FFAP capillary column) using nitrobenzene as the internal standard and dichloromethane as the extracting solvent. The CH_2Cl_2 solution (2 cm^3) was neutralized by one drop of concentrated NH_3(aq.). The pseudo-first-order rate constants were calculated from the slopes of the strictly linear ($r = 0.9998$–$0.999\,995$) correlation log ($S_t - S_\infty$) vs t, where S_t is the ratio of the GC integrals of the substrate and the internal standard at the time t. Each rate constant was measured twice and the values were equal within 3% at least (average 0.5%).

Product analyses. About 0.2 g of the substrate was stirred magnetically with 50 cm^3 of 1 M $HClO_4$(aq.) for 2.7 h (ca 1 $t_{1/2}$) and 24 h (ca 10 $t_{1/2}$) in the case of **1** and with the same volume of 5 M $HClO_4$(aq.) for 4 h (>10 $t_{1/2}$) in the case of **2** at room temperature in a tightly stoppered Erlenmeyer flask. The solution was extracted several times with CH_2Cl_2 and the combined organic solution

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Table 1. Rate constants of disappearance for 3- and 1-acetoxynortricyclanes (**1** and **2**) in aqueous perchloric acid at different temperatures and acid concentrations and in $DClO_4$ (D_2O)

Substrate	T (K)	$c(HClO_4)$[a] (mol dm^{-3})	X_0[b]	Log a_w[c]	k_Ψ (10^{-4} s^{-1})[d]
1	298.2	0.998	0.271	1.648	0.857 ± 0.003
	298.2	1.000			0.868 ± 0.009[e,f]
	298.2	1.492	0.381	1.626	1.226 ± 0.003
	298.2	1.968	0.487	1.572	1.564 ± 0.003
	298.2	2.479	0.611	1.522	1.959 ± 0.003
	298.2	3.020	0.758	1.474	2.388 ± 0.006
	298.2	3.496	0.906	1.430	2.797 ± 0.007
	298.2	3.914	1.052	1.388	3.228 ± 0.009
	298.2	4.472	1.271	1.322	4.000 ± 0.007
	298.2	4.970	1.491	1.254	5.093 ± 0.009
	298.2	5.483	1.740	1.174	6.727 ± 0.013
	298.2	6.185	2.118	1.048	13.30 ± 0.07
	278.7	6.508			1.582 ± 0.019
	288.2	6.468			5.29 ± 0.06
	298.2	6.428	2.259	1.000	17.52 ± 0.13
	298.2	6.428			17.63 ± 0.12[e]
	298.2	6.422			17.77 ± 0.10[g]
	308.2	6.384			54.39 ± 0.14
	298.2	6.993	2.604	0.880	41.67 ± 0.16
	298.2	7.563	2.977	0.748	102.9 ± 0.3
2	298.2	1.009	0.273	1.650	1.169 ± 0.009
	298.2	1.000			1.170 ± 0.018[e]
	298.2	1.003			1.90 ± 0.06[g]
	308.2	1.006			3.10 ± 0.02
	318.2	1.001			7.56 ± 0.04
	328.2	0.995			17.1 ± 0.3
	298.2	1.457	0.373	1.630	1.671 ± 0.008
	298.2	2.045	0.505	1.564	2.403 ± 0.004
	298.2	2.459	0.606	1.524	2.954 ± 0.006
	298.2	2.993	0.750	1.476	3.732 ± 0.010
	298.2	3.476	0.900	1.432	4.536 ± 0.010
	298.2	3.840	1.025	1.396	5.324 ± 0.010
	298.2	4.472	1.271	1.322	6.59 ± 0.03
	298.2	4.970	1.491	1.254	8.125 ± 0.014
	298.2	5.483	1.740	1.174	9.86 ± 0.05
	298.2	6.183	2.117	1.048	14.26 ± 0.05
	298.2	6.428	2.259	1.000	16.61 ± 0.06
	298.2	6.422			22.18 ± 0.06[g]
	298.2	6.458	2.276	0.994	17.13 ± 0.12
	278.7	7.084			2.83 ± 0.04
	288.2	7.038			8.97 ± 0.05
	298.2	6.993	2.604	0.880	26.43 ± 0.06
	298.2	6.993			26.6 ± 0.3[e]
	308.2	6.942			74.7 ± 0.3
	298.2	7.563	2.977	0.748	47.6 ± 0.2
	298.2	8.045	3.312	0.629	107.0 ± 0.4

[a] Temperature corrected.
[b] Excess acidity. [13]
[c] Logarithm of water activity. [12]
[d] Error limits are standard deviations.
[e] Calculated from the activation parameters (Table 2).
[f] M. Lajunen and V. Nieminen, unpublished results (1998).
[g] Measured in $DClO_4$ (D_2O).

was neutralized and dried by allowing it to flow through anhydrous K_2CO_3. The solvent was evaporated and the residue analyzed by GC and GC–FTIR spectroscopy, and the products were identified by comparing their retention times and spectra with those of the authentic 3-nortricyclanol **(3)** and 2-norbornanone **(4)**.[6]

RESULTS AND DISCUSSION

Rate constants, activation parameters, isotope effects and products. Reaction mechanisms

Rate constants of disappearance for 3- and 1-acetoxynor-

Table 2. Parameters of activation and solvent deuterium isotope effects and parameters of the excess acidity equations [Eqns (5)–(7)] at 298 K for the hydrolysis of 3- and 1-acetoxynortricyclanes (**1** and **2**) in $LClO_4$ (L_2O) (L = H or D), with standard deviations

Substrate	$c(LClO_4)$ (mol dm^{-3})	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J mol^{-1} K^{-1})	k_H/k_D
1	1.00	69.6 ± 0.4[a]	-89.3 ± 1.2[a]	0.68 ± 0.09[b]
	6.43	83.7 ± 0.3[c]	-32.3 ± 0.8[c]	0.985 ± 0.013
2	1.01	70.7 ± 0.6	-83.1 ± 1.8	0.61 ± 0.03
	6.43			0.748 ± 0.005
	6.99	77.1 ± 0.3[c]	-51.7 ± 1.1[c]	

Substrate	Mechanism	m^*_1	pK_{SH^+}	$m^{\neq}$[d]	Log (k_0/K_{SH^+})	Log $[k_{0,2}$ $(M^{-1}$ $s^{-1})]$
1	$A_{AC}2$	0.73 ± 0.04	-2.61 ± 0.10	0.96 ± 0.06	-7.593 ± 0.006	
	Ad_E2	0.79 ± 0.04	-2.19 ± 0.20	1.02 ± 0.05[e]		-7.25 ± 0.07
	$A_{AL}1$[f]	0.76 ± 0.05	-2.99 ± 0.12	1.91 ± 0.06	-6.80 ± 0.11	
2	$A_{AC}2$	0.80 ± 0.04	-2.36 ± 0.12	1.02 ± 0.06	-7.458 ± 0.006	
	Ad_E2	0.82 ± 0.03	-2.42 ± 0.09	0.82 ± 0.04[e]		-6.66 ± 0.07
	$A_{AL}1$[f]	0.77 ± 0.05	-2.52 ± 0.07	1.76 ± 0.05	-6.53 ± 0.10	

[a] M. Lajunen and V. Nieminen, unpublished results (1998).

[b] Ref. 5.

[c] Apparent values due to two competing reactions.

[d] $m^{\neq}_1$, $m^{\neq}_2$ or $m^{\neq}_3$ depending on the mechanism.

[e] $m^{\neq}_2 = m^*_2$ $m^{\neq}_2/1.80$. [13]

[f] The dominant reaction at the highest acid concentrations is assumed to be entirely the $A_{AL}1$ ester hydrolysis.

tricyclanes (**1** and **2**) in aqueous perchloric acid at different temperatures and acid concentrations and in $DClO_4(D_2O)$ are listed in Table 1. The rate constant (8.7×10^{-5} s^{-1}) for **1** as measured in 1.00 M $HClO_4$(aq.) at 298.2 K is in good agreement with that measured earlier under similar conditions (9.1×10^{-5} s^{-1})[3]. The rate constants for the two isomers are generally fairly close to each other, although **1** is a secondary and **2** a tertiary acetate. The activation parameters and solvent deuterium isotope effects calculated from the second-order rate constants [$k_a = k_\psi/c(HClO_4)$] are presented in Table 2. The entropies of activation (−89 and −83 J K^{-1} mol^{-1} for **1** and **2**, respectively), the enthalpies of activation (70 and 71 kJ mol^{-1}) and the isotope effects (k_H/k_D = 0.68 and 0.61) in 1 M $LClO_4(L_2O)$ (L = H or D) at 298 K are typical of the $A_{AC}2$ mechanism.[1] However, the same parameters when measured at a higher acid concentration (6.4 or 7 M), $\Delta S^{\neq} = -32$ and −52 J K^{-1} mol^{-1}, $\Delta H^{\neq} = 84$ and 77 kJ mol^{-1} and $k_H/k_D = 0.99$ and 0.75, respectively, are clearly higher. The differences are evidently due to a change of reaction from the ester hydrolysis ($A_{AC}2$ mechanism; Schemes 1 and 2) to the hydration of the cyclopropane ring (Ad_E2 mechanism; Schemes 1 and 2) with increasing acid concentration.[5] If a common change of the mechanism of ester hydrolysis from $A_{AC}2$ to $A_{AL}1$ (the acid-catalyzed unimolecular reaction via alkyl-oxygen fission)[1] took place with increasing acid concentration, the entropy of activation would become less negative than observed and the isotope effect would decrease rather than increase.[1,5]

3-Nortricyclanol **(3)** was the only product observed for 3-acetoxynortricyclane **(1)** in 1 M $HClO_4$(aq.), in agreement with the earlier studies,[3] but its level was clearly reduced at higher acid concentrations, when acetoxy-substituted norborneols and norbornanediols (not identified) were probably formed (Scheme 1; only one route, but evidently the most important,[5] has been presented). 2-Norbornanone (norcamphor, **4**) was the only observed product of 1-acetoxynortricyclane **(2)** at all acid concentrations studied (Scheme 2). Its formation from **2** and from 1-hydroxynortricyclane (**5;** Scheme 2) has been reported earlier in both alkaline and acidic media.[7,8]

Separation of two reactions by the excess acidity method

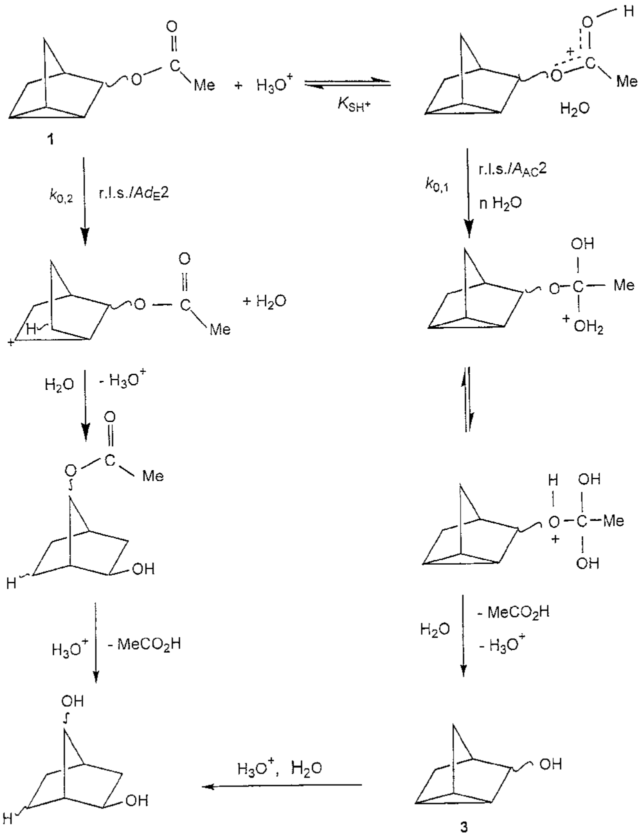
The separation of the two competing reactions can be made quantitatively by applying the excess acidity theory,[9,10] according to which the pseudo-first-order rate constant, k_ψ, obeys the equation

$$\log k_\psi - \log[c_S/(c_S + c_{SH^+})] - \log c_{H^+} - n\log a_w = m^{\neq}{}_1 m^*{}_1 X_0 + \log(k_{0,1}/K_{SH^+}) \quad (1)$$

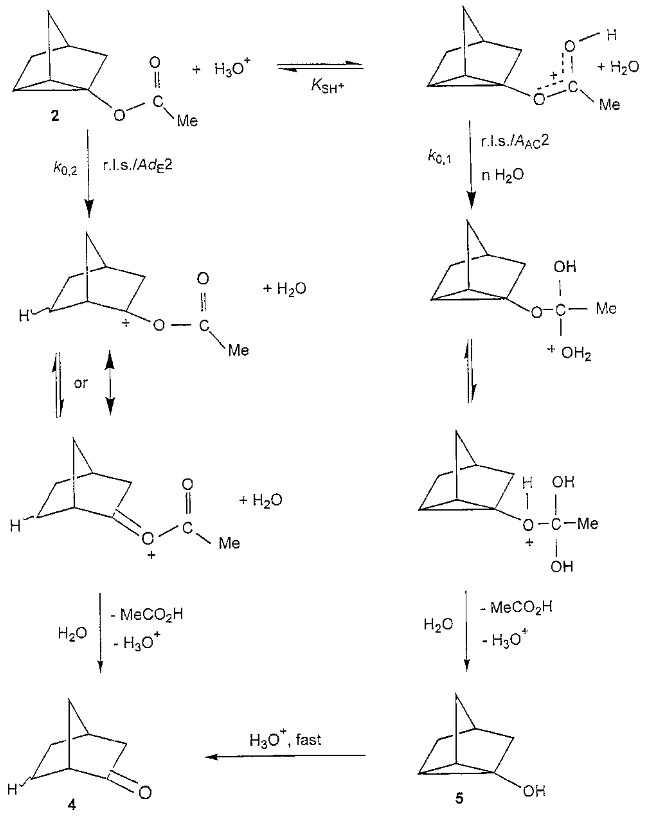
in the case of $A_{AC}2$ hydrolysis and the equation

$$\log k_\psi - \log c_{H^+} = m^{\neq}{}_2 m^*{}_2 X_0 + \log k_{0,2} \quad (2)$$

in the case of Ad_E2 hydration. In the latter reaction, partial protonation of the carbonyl oxygen, however, causes curvature of the ideally linear plot, $\log k_\psi - \log c_{H^+}$ $vs X_0$. This ‘side reaction’ can be taken into



Scheme 1



Scheme 2

account, when a linear equation[11]

$$\log k_\psi - \log[c_S/(c_S + c_{SH^+})] - \log c_{H^+} = m^{\neq}{}_2 m^*{}_2 X_0 + \log k_{0,2} \qquad (3)$$

is obtained. The correction term, $-\log[c_S/(c_S + c_{SH^+})]$, can be calculated with the equation[9]

$$\log(c_{SH^+}/c_S) - \log c_{H^+} = m^*{}_1 X_0 + pK_{SH^+} \qquad (4)$$

In these equations, c_S and c_{SH^+} are the concentrations of the unprotonated and protonated (on the carbonyl oxygen) substrate in the aqueous acid with concentration c_{H^+} [= $c(HClO_4)$], water activity a_w (the recent molarity-based log a_w values of Cox[12] are used, because their standard state is correct, 'a hypothetical ideal 1 mol dm^{-3} solution of water in water') and excess acidity X_0,[13] and n is the number of water molecules in the transition state.[9] The slope parameters $m^{\neq}{}_1$ and $m^{\neq}{}_2$ are indicative of the transition states of the two mechanisms and the slope parameters $m^*{}_1$ and $m^*{}_2$ depend on the site of proton attack, the former on the carbonyl oxygen and the latter on the cyclopropane ring ($m^*{}_2 = 1.80 \pm 0.10$)[12,13] and $k_{0,1}$ and $k_{0,2}$ are the medium-independent rate constants of the rate-limiting steps (r.l.s. in Schemes 1 and 2) of the two reactions. K_{SH^+} is the thermodynamic dissociation constant of the substrate protonated on the carbonyl oxygen.

$A_{AC}2$ hydrolysis is practically the only reaction at the three or four lowest acid concentrations. Thus the intercept parameter, $\log(k_{0,1}/K_{SH^+})$, can be estimated with Eqn. (1) from the rate constants measured under these conditions (Table 1) and from the following approximate values of the excess acidity parameters: $m^*{}_1 = 0.64$,[14–16] $m^{\neq}{}_1 = 1.00$[9] and $pK_{SH^+} = -3.43$ (for isopropyl acetate).[17] The approximate rate constant $k_{\psi,\mathrm{app}}(A_{AC}2)$ can be calculated at every acid concentration, and its subtraction from the corresponding observed k_ψ value gives the approximate $k_{\psi,\mathrm{app}}(Ad_E2)$. The hydration reaction is dominant at the five or six highest acid concentrations, when $k_{\psi,\mathrm{app}}(Ad_E2)$ obeys well the linear Eqn. (3) (e.g. $r = 0.9996$ for **1** and 0.998 for **2**, if $n = 2$). By extending the linear dependence to all the acid concentrations studied the improved approximations of $k_{\psi,\mathrm{imp}}(Ad_E2)$ can be evaluated and their subtraction from the observed k_ψ values gives improved $k_{\psi,\mathrm{imp}}(A_{AC}2)$ values. These rate constants can be used for the non-linear least-squares minimization (NLSM) according to the equation[18]

$$\log k_\psi(A_{AC}2) - \log c_{H^+} - n\log a_w = m^{\neq}{}_1 m^*{}_1 X_0 - \log[1 + (c_{H^+}/K_{SH^+})10^{m^*{}_1 X_0}] + \log(k_{0,1}/K_{SH^+}) \qquad (5)$$

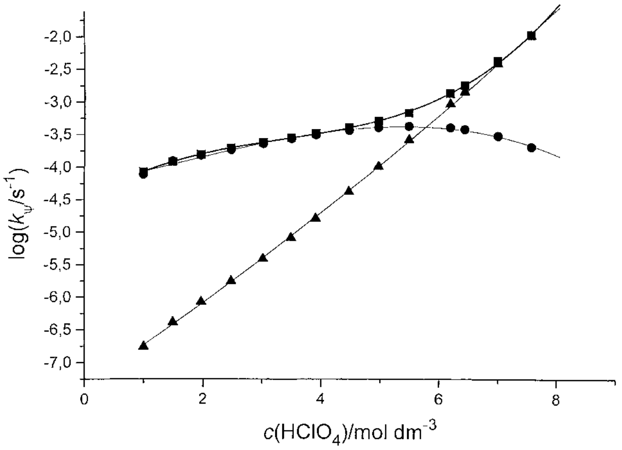


Figure 1. Logarithms of pseudo-first-order rate constants vs acid concentration for 3-acetoxynortricyclane (**1**) in HClO$_4$(aq.) at 298.2 K: ■, total disappearance; ●, $A_{AC}2$ hydrolysis; and ▲, Ad_E2 hydration

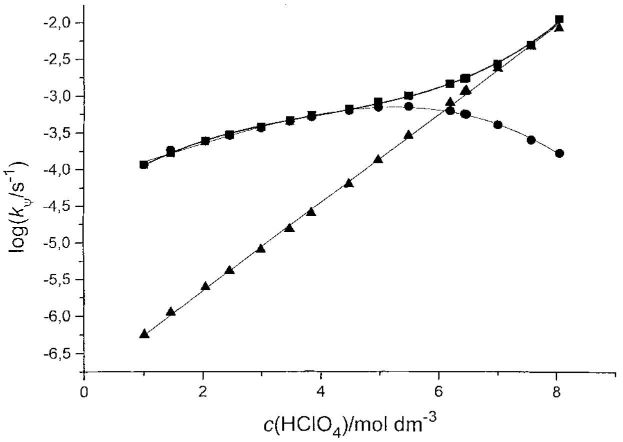


Figure 2. Logarithms of pseudo-first-order rate constants vs acid concentration for 1-acetoxynortricyclane (**2**) in HClO$_4$(aq.) at 298.2 K: ■, total disappearance; ●, $A_{AC}2$ hydrolysis; and ▲, Ad_E2 hydration

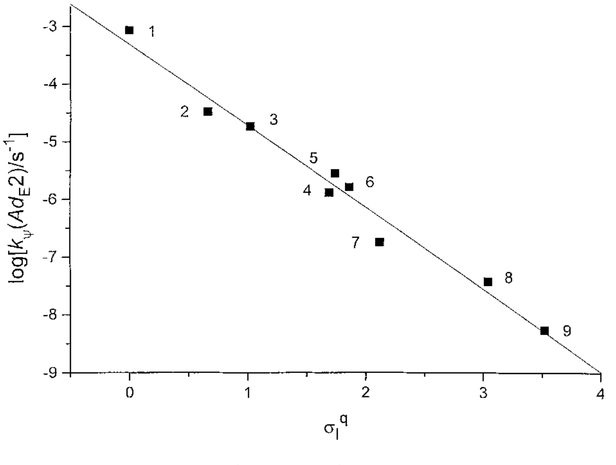


Figure 3. Logarithms of pseudo-first-order rate constants vs substituent constant σ_I^q of X for the Ad_E2 hydration of 3-X-substituted nortricyclanes in 1.00 M HClO$_4$(aq.) at 298.2 K: X = 1, H; 2, CH$_2$OH; 3, CH$_2$Cl; 4, COCH$_3$; 5, OH; 6, OCH$_3$; 7, OCOCH$_3$; 8, CN; and 9, NO$_2$

where improved values of the parameters $m^{\neq}_1$, m^*_1, pK_{SH^+} and $\log(k_{0,1}/K_{SH^+})$ can be obtained by iteration. They can be used as better approximate values (see above) and the whole iteration process is repeated until the values of the parameters no longer change markedly. The final best values are given in Table 2.

The NLSM iteration according to the equation[11,19]

$$\log k_\Psi(Ad_E2) - \log c_{H^+} = m^{\neq}_2 m^*_2 X_0 - \log[1 + (c_{H^+}/K_{SH^+})10^{m^*_1 X_0}] + \log k_{0,2} \qquad (6)$$

was also made with the final $k_\Psi(Ad_E2)$ values [$= k_{\Psi,obs.} - k_\Psi(A_{AC}2)_{NLSM}$] in order to estimate the values of parameters $m^{\neq}_2$ m^*_2, m^*_1, pK_{SH^+} and $\log k_{0,2}$. These parameters are also shown in Table 2. In this case the iterated values are, however, rather dependent on the initial estimated values of the parameters, probably owing to the small number of acid concentrations where the level of the Ad_E2 hydration is significant enough. Accordingly, these values may be less reliable than those for the $A_{AC}2$ hydrolysis in Table 2.

The iterative procedures worked well when the number of water molecules in the transition state of the $A_{AC}2$ hydrolysis was fixed at two, i.e. $n = 2$ in Eqns (1) and (5), but did less well or the excess acidity parameters obtained were exceptional values if $n = 1$ or 3. Two is the generally accepted number of water molecules in the transition state of the $A_{AC}2$ ester hydrolysis.[1,2,9,10,12]

Excess acidity parameters

The values of the excess acidity parameters in Table 2 seem, in the main, reasonable. The slope parameter m^*_1 for the protonation of the carbonyl oxygen, average 0.78 ± 0.04, is in agreement with that measured earlier.[14–16,18] The slope parameter $m^{\neq}_1$ for the $A_{AC}2$ hydrolysis, average 0.99 ± 0.03, is practically unity, as it should be.[9] The slope parameter $m^{\neq}_2$ for the Ad_E2 hydration of **2**, 0.82 ± 0.04, is typical of the acid-catalyzed protonation of the cyclopropane ring of nortricyclanes,[20] but that, for **1** 1.02 ± 0.05, seems too high, because generally $0 \leq m^{\neq} \leq 1$.[9] One reason may be the existence of some $A_{AL}1$ ester hydrolysis[1,2,12] in addition to the Ad_E2 hydration of the cyclopropane ring at high acid concentrations. The rate constant $k_\Psi(A_{AL}1)$ obeys the equation

$$\log k_\Psi(A_{AL}1) - \log c_{H^+} = m^{\neq}_3 m^*_1 X_0 - \log[1 + (c_{H^+}/K_{SH^+})10^{m^*_1 X_0}] + \log(k_{0,3}/K_{SH^+}) \qquad (7)$$

which is formally close to Eqn. (6), suitable for the Ad_E2 hydration, but generally gives $m^{\neq}_3$ values higher than unity (Table 2).[9,12] The activation parameters and the solvent deuterium isotope effects in 6.4 M $LClO_4(L_2O)$ (Table 2), however, show that the level of the $A_{AL}1$ hydrolysis cannot be large. Another reason may be some exceptional behavior of the acetyl group (enolization?), as was recently observed in the hydration of 3-acetylnortricyclane [preliminary values: $m^*_1 = 0.87 \pm 0.04$, $m^{\neq}_2 = 1.04 \pm 0.03$ and $pK_{SH^+} = -1.55 \pm 0.08$] (M. Lajunen and V. Mikkola, unpublished results). The average pK_{SH^+} value, -2.4 ± 0.2, evaluated for both **1** and **2**, shows that 1- and 3-nortricyclyl acetates are as expected more basic than isopropyl acetate ($pK_{SH^+} = -3.43$),[17] although the difference seems too great.

The parameters in Table 2 allow the estimation of the rate constants for both significant reactions, the ester hydrolysis and the hydration of the cyclopropane ring, with Eqns (5) and (6) at all acid concentrations used. These are presented in Figs 1 and 2 together with the observed total rate constants. The curves in Figs 1 and 2 seem reasonable. It is also possible to check the correctness of the rate constant $k_\Psi(Ad_E2)$ for **1**, because the corresponding values have been measured for several 3-X-substituted notricyclanes in $HClO_4$(aq.).[5,11,21–25] They are presented, as extrapolated to an acid concentration of 1.00 mol dm^{-3} and a temperature of 298.2 K, as a function of the substituent constant σ_I^q[26] of X in Fig. 3. This shows that the $k_\Psi(Ad_E2)$ value evaluated for **1** is in fair agreement with the others, although its level is only 0.2% of the total disappearance rate under these conditions.

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